

ATOMIC EMISSION AND LASER EXCITED ATOMIC FLUORESCENCE
STUDIES OF THE GLOW DISCHARGE FOR THE ANALYSIS OF
MICROSAMPLES

By

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Abstract of Dissertation Presented to the Graduate School
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ATOMIC EMISSION AND LASER EXCITED ATOMIC FLUORESCENCE
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Major Department: Chemistry

The glow discharge as an atomizer for atomic spectroscopy offers excellent advantages that have not been fully exploited. In this work fundamental studies about the sputtering process of liquid microsamples was investigated. This work was done by two different approaches: Atomic Emission Spectroscopy using a wavelength modulation technique for simultaneous background correction, and Laser Excited Atomic Fluorescence Spectroscopy. In the first approach, the sample holder was a cooled copper hollow electrode. The hollow depth as well as the atomizer operating parameters: current, voltage, and pressure were optimized in order to follow the temporal behavior of the analyte. In the second approach, the sample holder was a hot planar copper electrode. Here, the atomic excitation process was produced by a copper vapor pumped dye laser at a repetition rate of 6000 Hz, and the

fluorescence signal was collected at 90 degrees from the laser path. In the atomic fluorescence studies a comparison of the pulsed and non-pulsed operating modes of the glow discharge was carried out. Also, information about the vertical atomic distribution in the chamber area was obtained. Calibration curves and figures of merit for lead and gallium using the atomic emission system and lead using the atomic fluorescence system were determined. The effect of sodium chloride as a matrix interferant was investigated using both techniques. The results of these studies using the two approaches along with brief discussions about their theoretical aspects will be presented in this dissertation.

CHAPTER 1 HISTORICAL PERSPECTIVES

The discovery that the spectrum emitted by an atom was characteristic of that atom was the starting point of a new area in analytical chemistry called spectrochemical analysis. Arc and spark spectrography, both based on emission of radiation of excited atoms, were the first techniques which gained wide acceptance among the analytical community (1), performing both qualitative and quantitative elemental determinations.

Later, with the seminal papers of Walsh (2) and Alkemade and Milatz (3), a new analytical technique based on the absorption of resonance radiation by an atomized sample was shown to be an excellent approach for trace analysis of liquid samples in a wide variety of matrices. New advances in electronics, as well as the introduction of electrothermal vaporization by L'vov (4), placed atomic absorption spectrometry as the most sensitive procedure for elemental analysis during the 1960s and 1970s.

Wendt and Fassel (5,6) in the United States and Greenfield and coworkers (7,8) in the United Kingdom developed Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) as an analytical technique for trace metal analysis. ICP-OES offers the possibility of performing simultaneous or sequential elemental

determinations, with reduced matrix interferences and superior sensitivities and limits of detection for many elements (9) compared with flame AAS. These advantages made this alternative technique the method of choice for elemental determinations of samples.

The glow discharge (GD) is another excitation source for atomic spectroscopy. In 1916, Paschen studied a glow discharge configuration as a cathode discharge (10,11). The popularity of the other analytical techniques already mentioned, as well as some technical problems, especially the sample introduction system, overshadowed the progress and applications of the glow discharge as an atomizer. Several important and fundamental studies and applications of the glow discharge approach were described in the early literature for the analysis of solid samples (12-14) and to a lesser degree for determinations of several elements in previously dried liquid solutions (15-19).

An important development which increased interest in the development of new analytical applications of glow discharges was initiated in 1967 with the introduction by Grimm of a new low pressure discharge lamp which was used either as an atomic cell for elemental analysis or as a hollow cathode lamp source for atomic absorption spectroscopy (20). In 1972, Boumanns (21) reported an important evaluation of the Grimm type glow discharge for the determination of aluminum, copper, thallium, tungsten, and zirconium in solids using emission spectroscopy. Sputtering rates for those elements were determined at various operating conditions. In addition to studies that have been focused in the area of surface analysis (22-26),

other papers reported studies of the characteristics of the source (27-34), spectral interferences and a few have been oriented to the analysis of solutions. During the 1980s several important reviews on glow discharges were written by Pillow (35) and Swift (36), Ferreira and coworkers (37), Mavrodineau (14), Caroli (10), and Broekaert (38). All of them clearly showed the capabilities of the glow discharge as an analytical tool for spectrochemical analysis.

The atomic vapor in a glow discharge is produced through a sputtering process in which the atoms are ejected from the surface when highly energetic atoms or ions coming from the filler gas strike the cathode wall. Although most of the generated atoms are in the ground state, a small fraction are ionized (39). This observation led to extending the use of this atomizer as an ion source for mass spectrometry (40). In the last two decades, important work has been done by Harrison and coworkers in this area (41-44). A glow discharge mass spectrometric system especially designed for the analysis of surfaces is commercially available from at least one company (45).

A cathodic sputtering atomic source for atomic fluorescence spectroscopy was introduced by Gouch et al. (46). In their work, a high intensity hollow cathode lamp was used as the excitation source for the determination of nickel, chromium and copper. Although the limits of detection were only of the order of a part per million, their work demonstrated the feasibility of extending the use of the glow discharge in atomic spectroscopy to fluorescence where better selectivity is achieved.

The advent of laser technology in the 1960s with its special characteristics like high spectral irradiance, tunability, and monochromaticity opened a new avenue of

research in atomic fluorescence called Laser Excited (or Enhanced) Atomic Fluorescence Spectroscopy (LEAFS), where the analyte induced emission intensity depends on the laser irradiance. In the past 20 years, a number of publications report the use of different types of lasers as line sources for LEAFS using flames (47-49), inductively coupled plasmas (50-53), electrothermal atomizers (54-58), and glow discharges (59-64) as atom reservoirs.

The use of a low pressure glow discharge as an atomic cell for LEAFS has some unique characteristics that should be mentioned. First, the source produces sharp absorption lines. Second, quenching of fluorescence and chemical interferences are minimized by the presence of an inert gas. For these reasons the glow discharge behaves as a nearly ideal atom reservoir for LEAFS.

The glow discharge can be operated in a continuous or pulsed mode. When operated in the continuous mode, strong background emission reduces the detection capability of the determinations. The use of a pulsed glow discharge by Smith et al. (60) in which the laser (at 20 Hz) was triggered when the glow discharge was off permitting measurements of the fluorescence in a region where the background noise was totally eliminated. Using this approach, limits of detection of the order of femtograms were reported for lead using a glow discharge with a hollow cathode graphite electrode and a nitrogen and copper vapor laser pumped dye laser (61,65).

Research in LEAFS is still active. Many of these have been evaluated in excellent reviews published in the last few years (47,66). From these reviews, it is evident that the possibility of performing ultra-trace determinations in various

samples such as high purity materials, geological samples or biological fluids is very good.

According to several theoretical studies, LEAFS using a glow discharge as an atomizer also offers the possibility to detect single atoms (67). This situation has triggered the enthusiasm of several groups who are working in this direction using different types of laser systems.

Nevertheless, glow discharges with different geometries have been used for a long time and with purposes which span from qualitative and quantitative surface analysis of different types of alloys, to elemental quantitative analysis of solutions, either by measuring the emission or the absorption of the radiation by the atomized analyte and more recently the fluorescence produced after excitation with a strong monochromatic source like a laser. Lack of fundamental studies is evident, especially in the case of microsamples. Here, depending on the amount of analyte and the GD operating conditions, the signal reaches a plateau which may last several minutes before a decay is observed. This situation is a drawback for practical purposes where sample throughput is always of vital importance.

The aim of this dissertation is to report on fundamental studies carried out using a glow discharge as an atomic reservoir for the analysis of microsamples. The mass of analyte as well as the glow discharge operating parameters, pressure, current, and voltage, were optimized in order to follow the temporal behavior of sputtered atoms in a short period of time (seconds). The study was carried out using Atomic Emission Spectroscopy (AES) and LEAFS. For the emission experiments, a copper

hollow cathode electrode was eventually selected to avoid any possibility of losses through adsorption of the sample on the cathode walls and the GD was operated in the continuous mode. In addition, it was necessary to optimize the depth of the hollow cathode electrode in order to operate the discharge at currents of the order of 200 mA without affecting plasma stability. Moreover, an automatic background correction method was utilized to obtain the emission signal. For LEAFS studies, a hot planar copper electrode was the sample holder, and the atomizer was operated in either a continuous or a pulsed mode. Lead and gallium were selected as the analyte to be studied throughout this work.

CHAPTER 2 GLOW DISCHARGES

Introduction

The earliest observation of atomic emission in low pressure gases was reported at the end of the nineteenth century by Hittorf, Crookes and Geissler (10). However, it was Pashen who introduced the hollow cathode discharge in 1916 (11). Using helium at a pressure of 1 torr, Pashen noted that the glow formed when the discharge was initiated was confined within the cathode cavity made of aluminum foil.

Although, a clear acceptance of the glow discharges as an atomic reservoir for analytical purposes was delayed for reasons already mentioned in Chapter 1, the interest in low pressure discharges has persisted (43). It is worth mentioning here that the tremendous success of atomic absorption spectroscopy was due in great part to the development of the low pressure hollow cathode glow discharge lamps as line sources (68).

As was mentioned in Chapter 1, Grimm introduced a new version of a low pressure glow discharge with a planar cathode designed mainly for the emission analysis of solid samples. Since then, the use and evaluation of this discharge as an atomizer for spectrochemical analysis have increased dramatically as can be seen by the number of published reports about this source during the last twenty years.

Glow discharges have been used as atom reservoirs for qualitative or quantitative measurements in atomic emission, atomic absorption and atomic fluorescence spectrometry. Although it is very well suited for the analysis of surfaces and gases, liquid samples can also be analyzed after removing the solvent.

A detailed evaluation of the Grimm type glow discharge was reported by Boumans (21) in which the sputtering rates of aluminum, copper, molybdenum, nickel, thallium, tungsten, and zinc were determined in metals for various voltages, currents, and pressure combinations. Moreover, the sputtering rates of copper, zinc, and nickel were evaluated in several alloys, and the possibility of performing thin layer analysis using this technique was considered in this study.

Glow discharge has also been utilized to carry out depth profile quantitative analysis of surfaces of alloys such as stainless steels (23). By repeating the analysis using scanning electron microscopy, an accuracy equal to $\pm 4.9\%$ relative standard deviation was found. In another study, Berglund and Thelin (24), using a cooled hollow cathode electrode, reported the determination of traces of aluminum, arsenic, boron, calcium, chromium, manganese, molybdenum, niobium, nickel, lead, titanium, and tungsten in steels with precision between 1 and 3%. Bengton (69) developed an empirical equation to calculate the elemental concentration of manganese, nickel and iron in copper based alloys using a Grimm type glow discharge; his results were in good agreement with the certified values. Others studies concerning surface analysis using glow discharges have been published by Fang and Marcus (25) and Wagatsuma and Hirokawa (26).

The use of this low pressure source in conjunction with atomic absorption spectroscopy has allowed monitoring the atomic population of sputtered atoms in the discharge. Stirling and Westwood (13,22) measured the radial distribution of aluminum, nickel, and iron atoms in a cylindrical discharge chamber. They suggested that both atoms and molecules were sputtered from the cathode. Therefore, in their opinion, the determination of deposition rates using this approach was not possible.

Also using GD-AAS, McCamey and Niemczyk (70) concluded that the sputtering process is in general less prone to several of the interferences observed in the graphite furnace for elements like copper, strontium and lithium. For example, they found that the presence of sodium chloride in a relative concentration of 100:1 did not cause any interference in the determination of copper and lithium, but phosphoric acid and nickel nitrate at the same relative concentration significantly suppress the signal.

Winchester and Marcus (71) addressed the problem of analyzing nonconducting samples by GD-AAS. The determination of iron (III) and aluminum (III) oxides was possible after mixing them with metallic copper in a proportion of 1:9. Also, these compounds were determined in a NIST 96A bauxite with a precision of 8%. Their work demonstrated the possibility of using this technique to analyze other nonconducting materials like ceramics and glasses.

Fundamental Studies Using Glow Discharges

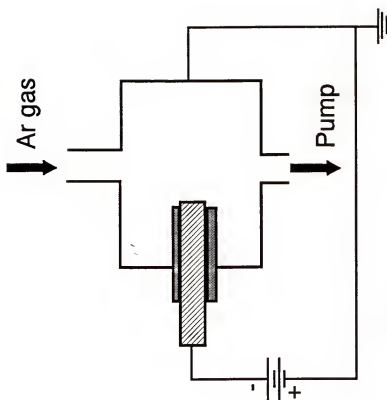
Low pressure glow discharges have been routinely used as lines sources for atomic absorption spectroscopy since 1952 (2) and on a smaller scale as

atomizers/excitation sources for analytical purposes since 1947 (72). A complete understanding of the fundamental processes occurring in glow discharges has not yet been accomplished. However, fundamental studies published in the literature in the last twenty-five years are an indication of the interest of some researchers in the elucidation of the glow discharge processes. In this direction, Ferreira and co-workers (37) reported the determination of gas kinetic temperatures ranging between 700 and 3700 K for a Grimm type glow discharge operated between 25 and 200 mA and electron number densities equal to 2×10^{14} and $3 \times 10^{14} \text{ cm}^{-3}$ respectively, obtained for 40 and 60 mA and 800 V of applied potential. A similar value for electron number density was found by Patel and Winefordner (31). McDonald (29), assuming local thermal equilibrium and 4300 K as the atomic and ionic temperature, found an electron density of $5.3 \times 10^{13} \text{ cm}^{-3}$ using the Saha equation; this value of electron density was close to the value found by Buger and Fink (73) using Stark broadening. All the results for electron densities in glow discharges were one or two orders of magnitude lower than values accepted for a system in local thermal equilibrium (9). Therefore, there is a consensus that glow discharge is a plasma which is not in local thermal equilibrium.

Direct Current Glow Discharges

A direct current glow discharge is obtained when a differential potential, usually between 400 and 2000 V, is applied between two electrodes enclosed in a low pressure glass or metallic chamber (Figure 2.1). Depending on the characteristics of

Figure 2.1. A direct current glow discharge with a planar cathode electrode.

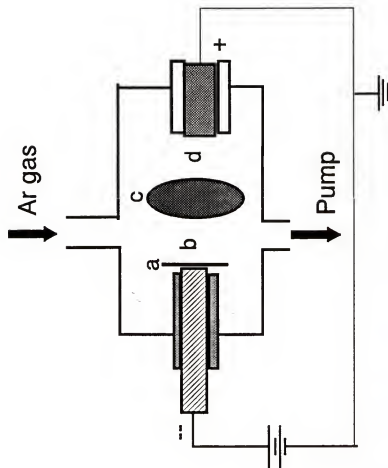


the current versus voltages behavior, different types of discharges can be obtained. A normal glow discharge is one in which the voltage remains constant even with an increase in current. Normally, this occurs for currents in the range of 10^{-4} A to 10^{-2} A. During this interval, the current density at the cathode remains constant, while the cathode area covered by the glow expands proportionally with the current (21). When the cathode is totally covered by the glow, any increase in the current also increases the current density and the voltage of the discharge giving rise to a region in which an abnormal glow discharge is produced. A further increase in the current finally produces an arc discharge.

Glow discharges used in spectrochemical analysis are operated under the conditions of an abnormal glow discharge at pressures which vary from 1 to 20 torr. When the anode is placed close to the cathode, the glow discharge contains four zones (Figure 2.2). The first is a thin dark layer very close to the cathode surface called the Aston primary zone. This is followed by a second zone called the Crookes or Hittorf dark space. Following the dark space, a third very intense luminous zone, called the glow region, is observed. The intensity of this region decreases toward the anode giving rise to a second dark space called the Faraday dark space.

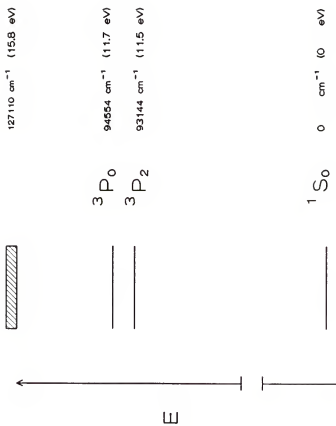
Any inert gas can be used as a filler gas in glow discharges. Argon and helium are the most frequently used. Argon has an ionization potential of 15.76 eV while helium has an ionization potential of 24.59 eV. Argon is preferred over helium because of its better sputtering efficiency. Argon also has two metastable states (Figure 2.3) at 11.5 eV and 11.7 eV which play an important role in several of the processes occurring in the glow discharge which will be treated in the next section.

Figure 2.2. Glow discharge zones (see text for explanation).



a, Aston zone; b, dark space; c, glow region; d, Faraday dark space

Figure 2.3. Argon metastables levels.



Glow Discharge Processes

The degree of ionization (fraction of ionized atoms) in a glow discharge is of the order of 10^{-4} to 10^{-6} (42). This means that basically the discharge is formed by neutral atoms. However, the system is also characterized by the formation through gas phase collisions of other species such as ions, electrons, excited neutral atoms, molecules and photons. Table 2.1 lists the primary types of processes occurring in an argon glow discharge and responsible for the behavior of the discharge as an atomizer for atomic spectroscopy.

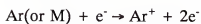
Several of the collisional processes described in Table 2.1 produce atoms in the excited states. It is precisely the emission of energy of these species that gives rise to the strong luminosity of the glow region. If the relaxation process occurs in several transitions, the lifetime of the species may last several microseconds. Also from Table 2.1, electron impact ionization is the most important of the inelastic collisions because it generates most of the electrons required to maintain the glow discharge.

Other processes not included in Table 2.1 are recombination processes which take place through collisions among different species or against the chamber walls and photoionization processes which were reported to play a minor role in the production of analyte ions in a 2 torr neon glow discharge (42). These processes explain the experimental fact that the ion and electron density in the gaseous system do not increase limitlessly.

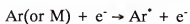
TABLE 2.1

Gas phase collision in an argon abnormal glow discharge

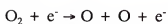
Electron impact ionization:



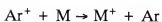
Electron impact excitation



Electron impact dissociation



Charge transfer



Metastable collisions

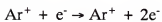
1. Penning ionization



2. Metastable-Metastable ionization



3. Electron-Metastable Ionization



Key: Ar, neutral Argon; Ar^* , metastable argon; M, analyte atom; M^* , analyte ion; O_2 , oxygen molecular; O, oxygen atom; e^- , electron

The Sputtering Process

When the glow discharge is in operation, neutral atoms and positive ions of the supporting gas which are further accelerated by the strong electric field generated by the applied potential collide with the cathode. This may result in the ejection of atoms from the electrode material in a process called sputtering. In addition to atoms, secondary electrons can also be produced when high energy argon ions approach the cathode. The atoms ejected from the cathode cross the dark space by diffusion and reach the glow region where they are excited or ionized through interaction with ions, electrons, neutral, or metastable gas atoms.

The cathode can be the sample itself, as in the Grimm type atomizer, or a graphite or metallic hollow electrode as in the Pashen design. The main limitation with respect to the sample is that it must be electrically conducting. Otherwise, it has to be mixed with a conducting material such as copper or graphite before analysis.

Pulsed and Radio-Frequency Glow Discharges

In addition to the direct current mode, the glow discharge can be operated in a pulsed mode or a radio-frequency mode. When operated in the pulsed mode, significant enhancement in the emission intensity of the analyte as well as a reduction in the background noise are observed. This characteristic has been well exploited when the discharge is used as a line source for AAS (74). When used as an atomizer

for laser excited atomic fluorescence spectroscopy, the pulsed mode offers an additional advantage which will be discussed in chapter 4.

The use of glow discharges driven by a high frequency power supply is of common use in sputter deposition or plasma etching when it is necessary to cover an electrode with an electrically insulating material (39). The use of this type of discharge in optical spectroscopy offers several advantages. First, it permits direct analysis of nonconducting materials (glass, ceramics). Second, the atomizer can be operated at very low pressures (less than 1 torr) reducing collisional redeposition of sputtered atoms and the formation of chemical species like metallic oxides. Third, the RF glow discharge is more efficient than the DC glow discharge in promoting ionization and sustaining the discharge (42). Fundamental studies on RF glow discharges are underway by Harrison et al. (43).

Analysis of Solutions

Compared with the analysis of solid samples, the application of the glow discharge to the analysis of solutions is more difficult as these must be deposited on an appropriate surface and dried prior to the initiation of the discharge. In most of the applications, graphite has been the cathode material; however, metallic electrodes of copper, aluminum, and stainless steel also have been utilized (18). Earlier publications report the use of helium glow discharge operated at 15 torr and currents higher than 300 mA as an atomizer for spectrographic elemental determinations (15-17). Most recently, papers have reported the use of argon as the filler gas for

elemental determinations using atomic emission (18,19,75-78), absorption (79) or fluorescence spectroscopy (61,68,80). The feasibility of using the glow discharge for the analysis of biological samples was demonstrated by Harrison and Prakash (18) and Caroli et al. (75). Harrison and Prakash (18) reported the determination of lead in hair and liver with LOD between 2 and 8 $\mu\text{g/g}$. Caroli et al. (75) reported the determination of aluminum, arsenic, calcium, copper, gallium, and zinc in kidney, liver, brain and blood of mice. These studies indicate that the glow discharge did not appear to be significantly prone to matrix effects. Attempts to perform analysis of solutions by AES with continuous sample introduction in the glow discharge was first addressed by Brackett and Vickers (81-82) who determined a LOD of 0.9 ppm for lead and suggested the possibility of using the atomizer as a detector for liquid chromatography. In a recent publication, Strange and Marcus (83) used an HPLC particle beam interface as a sample introduction system of liquid samples into a glow discharge. Preliminary atomic emission results were presented but no quantitative results were obtained because of incomplete atomization of the sample and memory effects.

CHAPTER 3

STUDIES OF THE SPUTTERING PROCESSES OF MICROSAMPLES BY GLOW DISCHARGE-ATOMIC EMISSION SPECTROSCOPY WITH WAVELENGTH MODULATION

Introduction

The aim of this work was to carry out a study of the sputtering process in a low pressure glow discharge using a metallic and cooled hollow cathode electrode. Analyte signals were measured by atomic emission spectroscopy. A system was set up and optimized to analyze microsamples after evaporation of the solvent. A background correction method in which the signal was modulated was implemented in order to obtain the analyte signal. The temporal behavior of lead samples was followed at different voltage-current and pressure conditions. After the system was optimized, the sensitivity was evaluated for lead and gallium where detection limits of the order of picograms were obtained for both elements. The effect of sodium chloride as a matrix interference as well as the effectiveness of ammonium nitrate as a matrix modifier were evaluated in the case of lead.

Glow Discharge Atomic Emission Spectroscopy with Wavelength Modulation

The emission of radiation of specific energy previously supplied from outside to the atom is the basis for Atomic Emission Spectroscopy (AES) (84). This process

involves an electron of the outer shell of the atom absorbing a specific amount of energy that places the atom in an excited state. Because the atom to be excited must be in the gas phase, most samples are subjected to preliminary steps before being vaporized and atomized to enhance atom formation. For example, the combination of a nebulizer-spray chamber and a flame or an inductively coupled plasma has succeeded as a continuous sample introduction system for liquid samples by AES despite a low transport efficiency (85) which requires several milliliters of sample to perform the analysis.

The use of a low pressure glow discharge as an atom reservoir for atomic spectroscopy presents several advantages over other approaches: sharper spectral lines, lower background emission, and reduced quenching processes make this source an excellent atom reservoir not only for atomic emission but for fluorescence measurements as well. However, when the glow discharge is used as an atomic emission source for the analysis of microsamples, there exists a serious difficulty in making an accurate background correction. This situation is worse if the signal has to be amplified several orders of magnitude. In this case, spectral lines due to other species like the filler gas, the cathode material, or molecular bands (for example, the $\text{OH}^\cdot$ which covers the region from 280 to 400 nm) interfere with the measurement of the intensity of the spectral line of interest. This situation could be overcome using a high resolution monochromator as Buell demonstrated (86). This work used another approach based upon the modulation of the wavelength as described by Snelleman et al. (87) for the determination of alkali and alkali earth elements by

flame emission spectroscopy. The utility of this approach also was demonstrated by Verrept and coworkers (88) in the determination of lead in the presence of aluminum by electrothermal vaporization-inductively coupled plasma atomic emission spectroscopy (ICP-AES). The procedure involves the measurement of the derivative of a spectrum with respect to wavelength. To accomplish this, the wavelength is modulated sinusoidally over a small interval $\Delta\lambda$ centered on the desired line, called the modulation interval (89). In practice, this is achieved by repetitively and rapidly scanning back and forth over the modulation interval with the help of a synchronized vibrating quartz plate which is placed inside and in front of the entrance or exit slit of the monochromator. The resulting AC signal is electronically isolated with a lock-in amplifier that also assists in filtering low frequency noise which originates from the source.

Instrumentation

Figure 3.1 shows the system that was set up in the laboratory to carry out the atomic emission studies relating to the temporal behavior of the sputtered atoms. Basically, it consists of the following sections: the source (the glow discharge), the optical collection system (a convex lens), the dispersion system (monochromator), the wavelength modulation device, and the detection system (photomultiplier tube, current to voltage converter amplifier, lock-in amplifier and computer).

Figure 3.2 shows glow discharge chamber. It was made from a six-way 2.25 in. flange vacuum cross from Huntington Lab., Inc. (Mt. View, CA). It was placed

Figure 3.1. Glow discharge-Atomic emission system.

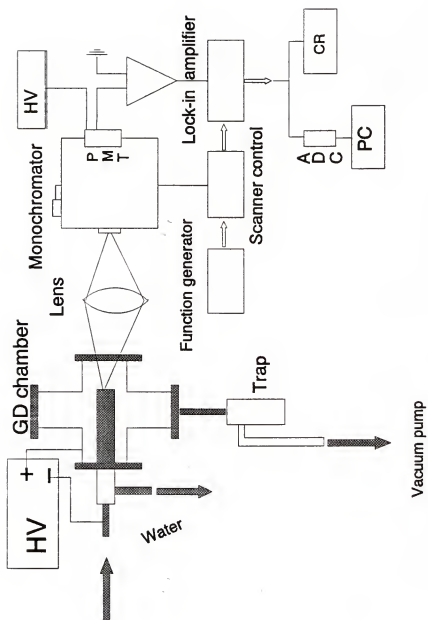
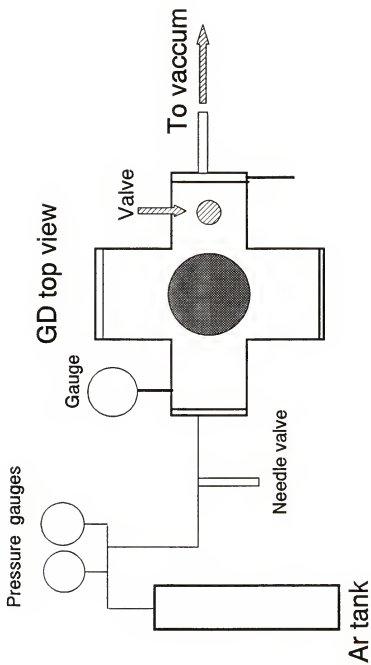


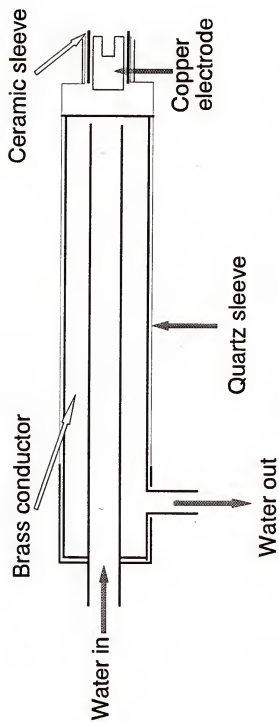
Figure 3.2. Glow discharge chamber (top view).



on an X-Y translational and a vertical stage to facilitate its optical alignment. One port was connected to the vacuum pump with a trap in between. When the source was operated, the trap was cooled to approximately -78°C with a mixture of acetone-dry ice to minimize any contamination by oil vapor from the pump. A second port was connected to a butterfly valve for opening the chamber to atmospheric pressure. The third port was used to measure the chamber pressure with a Bourdon type mechanic vacuum gauge or a capacitance manometer (MKS Instrument, Model Baratron 221A, Burlington, MA). Two others ports were used for the cathode holder and for introduction of the fill gas, argon in this case. The sixth and last port was a quartz window from where the emission signal emerges to be collected and focused at the monochromator. The cathode holder, as seen in Figure 3.3, was made from a rod of brass and machined in such a way as to permit water cooling of the cathode and sample holder. The rod was insulated from the chamber by means of a quartz sleeve that was fitted over the cathode holder. When apiezon was used to seal the quartz sleeve to the rod, the electrode cavity was contaminated with a black residue when the source was operated. This situation was eliminated by replacing the apiezon by a polymeric resin (Torr seal, Varian, Lexington, MA).

The discharge was initiated by a high output power supply (Hipotronics, Inc., Model 803-330, Brewster, NY) with the capability to deliver potentials up to 3000 V and currents up to 400 mA. The positive end of the power supply was attached to the stainless steel chamber and the negative end was connected to the end of the cathode holder. A $2.5\text{ k}\Omega$ resistor was placed in series with the chamber to limit

Figure 3.3. Glow discharge cathode assembly.



the current through the discharge. A rotary vacuum pump was used to evacuate the chamber to a pressure below 0.1 torr, and to maintain the chamber pressure at the working conditions, usually less than 10 torr. A needle valve was placed close to the chamber gas inlet to control the gas flow into the chamber as seen in Figure 3.2.

The optical collection and dispersion system consisted of a 7.5 in. focal length convex lens placed in between the quartz window of the chamber and the entrance slit of a 0.3 m McPherson monochromator model 218 with a grating of 1200 grooves per mm, an effective aperture of $f/5.3$, and a wavelength accuracy of ± 0.1 nm.

In order to perform the automatic background correction, a rectangular 2.5 cm by 5 cm quartz plate 2 mm thick was placed inside the monochromator and in front of the monochromator exit slit. The plate was mounted in a rotating mechanical oscillator located on the top of the monochromator cover and its frequency, angle, and modulation was controlled by a system formed by a Wavetek signal generator, a CCX101 General Scanning Inc. scanner control, and a lock-in amplifier model 5101 (EG&G Princeton Applied Research). The plate was operated at a frequency of 100 Hz and for an angle of vibration of approximately 5° .

A wavelength interval of 0.45 nm was scanned. The signal was detected by a fast response photomultiplier tube (R955, Hamamatsu Corp.) operated at -950 V. The output current was amplified by a current-to-voltage converter (Keithley Model 427) and then was input along with a reference signal to the lock-in amplifier where it was further amplified and filtered to finally be sent to an analog to digital converter (Model SR245, Stanford Research System, Palo Alto, CA) and stored in a personal

computer for data processing. Also, the analog signal was recorded with a strip chart recorder (Fisher Recordall, Series 500, Omniscrite, Austin, TX).

Results and Discussion

To study the temporal behavior of the sputtered atoms by GD-AES, it is necessary to remove all the analyte from the cathode in the shortest period of time and with no losses due to adsorption in the cathode material. To fulfill the first condition the size of the sample as well as the operating parameters of the glow discharge, were optimized. Previous studies have demonstrated that the sputtering of 10 to 20 μg from a graphite hollow cathode electrode lasted several minutes when voltages of the order of 1000 V were applied to the discharge at a pressure of 10 torr (61). The second condition could be achieved either by using pyrolytic or metallic coated graphite electrodes or simply metallic electrodes.

Attempts were made to make pyrolytically coated graphite electrodes using the approach of Manning and Ediger (90) developed for the cylindrically shaped graphite tubes of common use in electrothermal atomizers but technical problems gave rise to fruitless results. The use of a small platinum cup as a sample holder, which was inserted into the hollow of the graphite electrode, also was considered but the impossibility of keeping the cup inside the electrode when the chamber was under vacuum made this approach infeasible. Several platinum coated graphite electrodes were made by redeposition of a large amount of platinum. At pressures of 10 torr and a current of 40 mA more than 50% of the ejected platinum atoms are

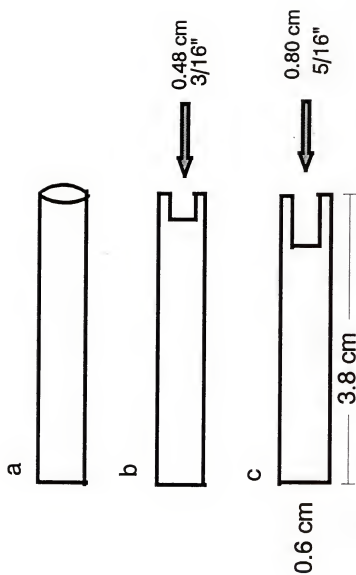
sputtered back forming a layer that totally covers the hollow cavity. The main disadvantage of these electrodes was that the platinum layer was not immune to the sputtering process and a rapid deterioration of the surface was observed that depletes the platinum after approximately five experiments. In addition, the use in microanalysis of any type of graphite electrode is totally inadequate because of the effect of water contained in the electrode upon the plasma conditions that quenches the metastable argon, reducing the glow intensity and therefore the performance of the atomizer.

Metallic Electrodes

The use of metallic electrodes as sample holders for cooled hollow cathode electrodes in glow discharge-atomic emission spectroscopy has also been reported in the literature. In the selection of the appropriate electrode material, special considerations should be taken into account. According to Czakow (91), the metal should have 1) a spectrum with few spectral lines and a negligible background; 2) good thermal conductivity and high melting point; 3) low susceptibility to cathode sputtering; 4) chemical resistance; 5) good machinability; 6) lack of toxicity, and 7) high purity and low cost.

In this work, high purity copper (Goodfellow Metals, Cambridge LTD, England), which has some of the properties mentioned above, was selected to make the electrodes. Planar and hollow electrodes as shown in Figure 3.4 were properly machined to fitted inside the brass cathode holder. The diameter of the hollow was

Figure 3.4. Hollow copper cathode electrodes.



4 mm and initially the depth was 5 mm (3/16 in) and later was changed to 8 mm (5/16 in) to work at currents higher than 150 mA.

The glow discharge was stable when operated with the planar electrode at currents lower than 20 mA and a pressure of 1 to 10 torr. At these operating conditions, no analyte emission signal was observed for lead. This could mean that the sputtering rate was too low and the analyte atomic population in the glow region which was excited was not enough to produce a detectable signal above the background emission from the source.

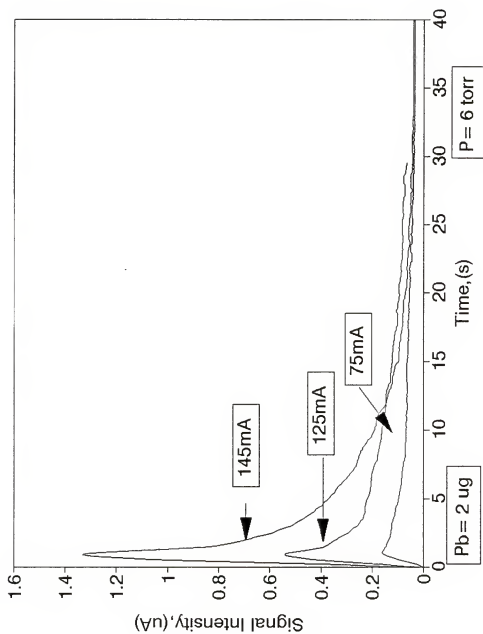
To increase the sputtering rate, it is necessary to increase the number of energetic electrons, argon ions, and argon metastables in the system. This could be achieved by operating the glow discharge at higher powers (higher currents and voltages). The use of metallic hollow electrodes where the surface area exposed to the discharge was greater than in the planar electrode offered the following advantages: first, it permitted operation of the glow discharge at higher voltages and currents; second, the plasma stability was superior compared to the one produced by the planar electrode; and finally, the glow region was confined inside the hollow and therefore the population of sputtered atoms were concentrated in the same region, increasing the analyte residence time, and therefore the excitation probability. In this way, intense emission lines were observed.

The 5 mm (3/16") depth hollow cathode electrode made it possible to follow the temporal behavior of dried solutions of lead nitrate. The use of the same volume of sample of different concentrations gave better reproducibility than using different

volumes of the same concentration. When samples containing more than $1.00\ \mu\text{g}$ were analyzed, the electrode was rinsed first with 5% nitric acid and then with ultrapure water to remove any lead that could be deposited after switching off the discharge. Each determination was done using the same scheme which included the following steps: 1) the electrode was pre-burned for 2-3 min to clean up the copper surface of any possible contaminant-like copper oxides; 2) the sample volume of $0.50\ \mu\text{L}$ was placed carefully at the bottom of the electrode using a $2.00\ \mu\text{L}$ micropipet (Rainin Instrument Co., Inc., Woburn, MA) with a relative accuracy of 5%; 3) the sample was dried using an infrared lamp for 3-4 min; 4) the electrode was fitted inside the cathode rod and a ceramic sleeve was inserted from the top to cover about 20% of the electrode which remained out of the rod housing; 5) the chamber was evacuated to less than 0.1 torr for 2 min and the pressure was set to the desired value; 6) the discharge was initiated at a determined voltage using a switch, and the signal was recorded and stored in a personal computer.

The 280.3 nm lead spectral line was used in this study and it was selected experimentally as the line which produced the strongest emission by placing solid lead in a graphite electrode and scanning the monochromator between 200 nm and 300 nm. Figure 3.5 shows the temporal behavior when samples containing $2\ \mu\text{g}$ of lead were analyzed at 75 mA, 125 mA, and 145 mA respectively, and at pressure of 6 torr. The shapes of the curves show a fast and linear initial rate of emission followed by an exponential decay that lasts for a few seconds. A 6 torr pressure was selected as the glow discharge pressure after examination of the signal to noise ratio

Figure 3.5. Lead temporal behavior at three different currents. (Pb mass = 2 μ g, P = 6 torr, electrode depth = 5 mm)



obtained by placing solid lead in a graphite electrode. These results clearly showed the effect of increasing the applied power to the glow discharge on the intensity of the emission signal where a signal enhancement of about 13 times was obtained by increasing the current only 2.6 times.

Figure 3.6 shows lead emission signals for different masses at different currents. Although these calibration curves do not represent the best sensitivities reached in this study (to be discussed later in this chapter), they are important because they suggest that in this range of masses, better linearity is obtained if the glow discharge is operated at currents lower than 145 mA.

Attempts were made to work at higher currents to increase the sputtering rate and degree of excitation but arcing problems prohibited working at currents above 150 mA. This situation happened when the electrode area was unable to support the operating current. To work at higher current densities, it was necessary to increase the electrode area, and, in this case, this was done by increasing the electrode depth. For this reason, the 5 mm depth electrode was replaced by a 8 mm depth which experimentally accepted currents as high as 200 mA at a potential of 1300 V without affecting the plasma stability.

The optimization of the glow discharge operating pressure was carried out using 1.000 μg of analyte and examining the temporal behavior of the emission signal at a current of 190 mA and a voltage of 1200 V (228 W) and at pressures spanning from 1 torr to 10 torr. Figure 3.7 shows the result of this study and they sustain the selection of two torr as the working pressure with the 8 mm depth electrode. It was

Figure 3.6. Lead atomic emission signals for 4, 8, and 16 μg at five different currents.

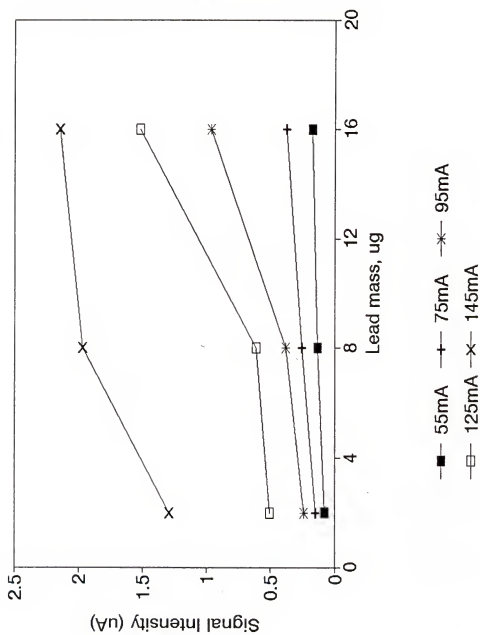
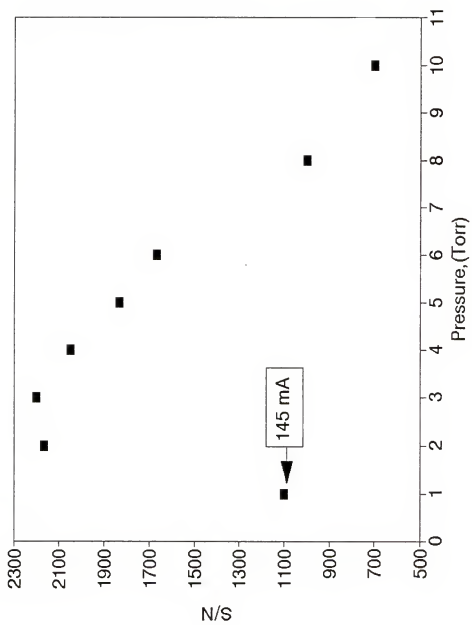


Figure 3.7. Variation of the lead signal to noise ratio with pressure.



impossible to obtain the temporal behavior at 190 mA for a pressure of 1 torr because the plasma was not stable for these conditions. Another important consideration in the choice of 2 torr as the optimal pressure for this work is the absence of any pressure effect on the exponential decay of the signal. This effect was present at a pressure of 3 torr and above and was characterized by a shoulder in the signal as is shown in Figure 3.8.

To explain the effect of pressure on the shape of the temporal behavior of the analyte signal, it is necessary to consider the effect of this parameter on analyte diffusion. It is well established that by increasing the gas pressure, the gas mean free path is reduced, and the diffusion coefficient decreases (92). Therefore, if the residence time of the analyte atoms in the glow region is greater, the probability for multiple excitation before diffusion from the glow is greater at higher pressures. The other point that should be considered is the ejection of analyte clusters from the surface (37,69). These clusters could then be dissociated in the glow region and produce a shoulder in the peak. The dissociation of clusters is enhanced by the low diffusion rate of the analyte in the glow region.

A study of the temporal behavior of the emission signal at the nanogram level of analyte also was addressed in this work. For example, Figure 3.9 shows the result obtained when 50 ng of lead were subjected to the discharge. The figure shows that the analyte was totally sputtered in about one second, and the signal peak maximum was reached in approximately 0.1 s. This result also demonstrated the feasibility of

Figure 3.8. Lead temporal behavior at 10 torr. (Pb mass = 1.000 μg , I = 190 mA)

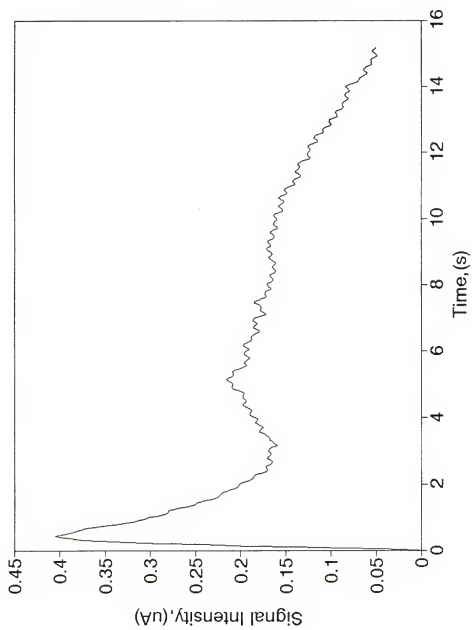
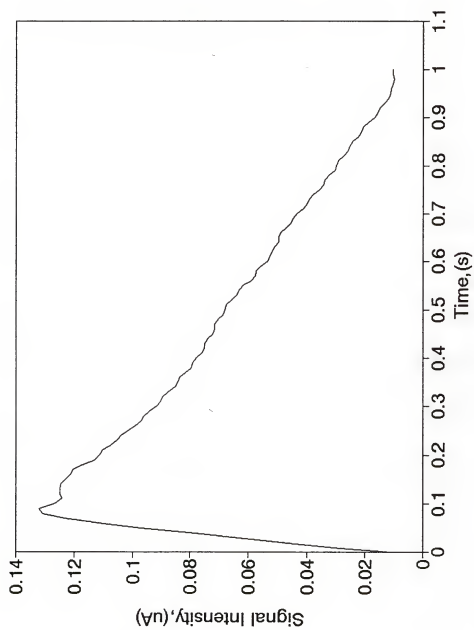


Figure 3.9. Lead temporal behavior for 50 ng at 190 mA. (electrode depth = 8 mm).



determining quantitatively lead in microsamples at nanogram levels by GD-AES. In order to make a calibration curve and determine the analytical figures of merit for lead, the emission signals of various other amounts of lead were determined at least in triplicate and with precision ranging from 7% to 20%. These results appear in Figure 3.10. By increasing the sensitivity of the lock-in amplifier and the gain of the current to voltage converter, the noise was determined to be 2.6 nA RMS. Figure 3.11 indicates the signal-to-noise ratio as a function of amount of analyte and Figure 3.12 is a log-log representation of the analytical calibration curve. A slope of 1.0 is obtained if only the first three points are considered. This means that the curve presents good linearity in this range of concentrations with a linear dynamic range of about two orders of magnitude. The curvature at high amounts is probably a result of self-absorption and self-reversal.

The possibility of having self-absorption and self-reversal in the glow discharge has been discussed by several authors (37,69). This phenomenon could explain the curvature at amounts higher than 400 ng. The fact that the analyte is sputtered off in a few milliseconds, and it is confined in a volume 0.1 cm^3 inside the hollow for a few milliseconds may create the conditions for the analyte to undergo self-absorption and self-reversal.

The limiting noise in these experiments was due to the background emission generated by the glow discharge. The limit of detection calculated on the basis of this noise, the slope of the calibration curve in the linear part, and a statistical factor of 3, was equal to 900 picograms. This value is similar or better to other values

Figure 3.10. Lead analytical calibration curve at 190 mA. ($P = 2$ torr, electrode depth = 8 mm).

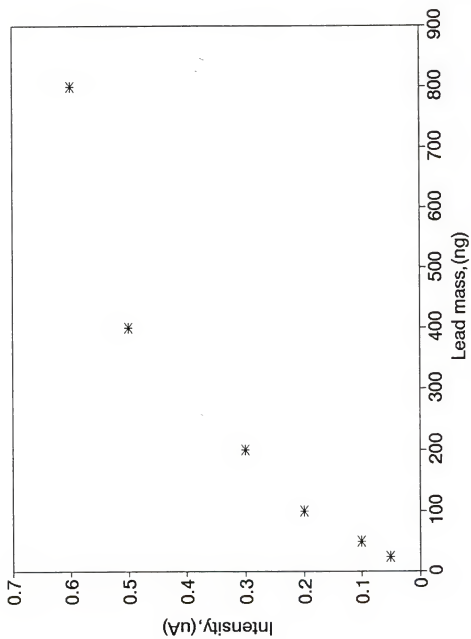


Figure 3.11. Lead signal to noise ratio for different masses at 190 mA.

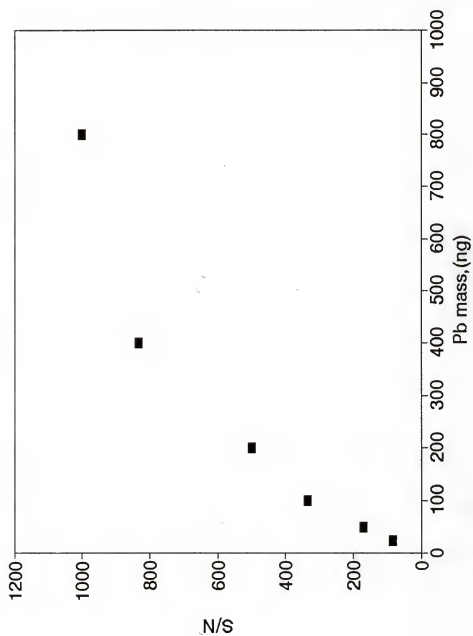
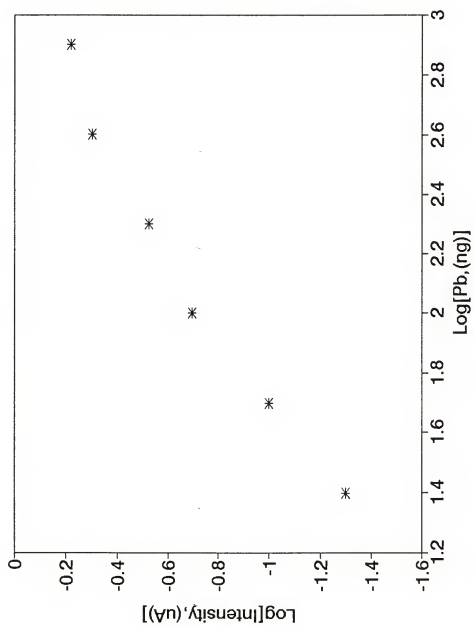


Figure 3.12. Log-log plot of the lead analytical calibration curve at 190 mA.



reported in the literature using this atomizer at other operating conditions. In addition, the limit of detection achieved in this work is about three or four orders of magnitude greater than the theoretical sensitivity calculated to be 10^{-13} g by Mandelstam and Nedler (93) for atomic emission determinations with the glow discharge as the atom reservoir but assuming that the minimum measurable line intensity is determined not by the source but for the average fluctuations of the dark current of the detector that they assumed as 1 pA.

Study of Matrix Interferences

Matrix interferences are a common occurrence in several analytical techniques which use flames (82), furnaces (94), or inductively coupled plasmas as atomizers for atomic spectroscopy (9). Its impact in glow discharge spectroscopy has been scarcely considered and the few data about this phenomenon are not in complete agreement. For instance, Caroli et al. (75) reported that the glow discharge tends to be substantially independent of matrix effects compared with arc emission spectrography and atomic absorption spectrometry; on the other hand, McCamey and Niemczyk (70), Vamos et al (95), and Falk (96) found a reduction of the signal intensity of several elements due to other species present in the matrix. These results were considered in the present work where an evaluation was done on the effect of chlorides, the most common interferer found in the determination of lead by atomic spectroscopy.

To carry out this study, 50 ng of lead were mixed with different amounts of sodium chloride and the temporal behavior of the sputtered atoms was measured. The operating voltage was 1100 V, the current was 190 mA and the pressure 2 torr. The results showed that when the mass concentration of sodium chloride was the same, twice or ten times the analyte mass concentration, no matrix interference was observed. This can be seen in Figures 3.13, 3.14, and 3.15. However, a strong reduction of the emission signal was observed when the sodium chloride mass concentration was 100 or 200 times higher than the lead mass concentration. These observations are shown in Figures 3.16 and 3.17 and all the results are condensed in a plot as seen in Figure 3.18.

Matrix Modifiers

The concept of matrix modifiers in electrothermal atomization-atomic absorption spectroscopy (ETA-AAS) to eliminate matrix interferences was introduced by Ediger et al. (97). He demonstrated that in the analysis of saline water the addition of ammonium nitrate helped in the removal of the sodium chloride matrix during the charring cycle so that an extraction procedure was not required. Since this first application of matrix modifiers, an increasing number of papers have reported the use of this approach with different chemical species to minimize many interferences. Substances like nitric acid, ammonium nitrate, phosphoric acid, ascorbic acid, and palladium salts (98,99) have been used with positive results.

It is well known that chloride salts when present in the analytical samples at concentration of the order of 1% or higher, produce a negative effect in the

Figure 3.13. Temporal behavior of 50 ng of lead in presence of an equal amount of NaCl.

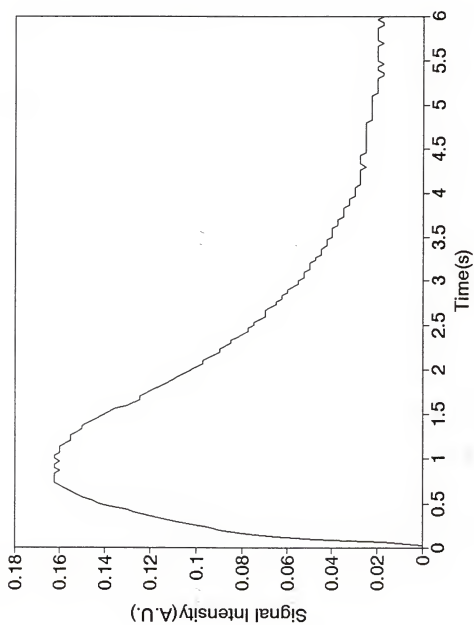


Figure 3.14. Temporal behavior of 50 ng of lead in presence of 100 ng of NaCl.

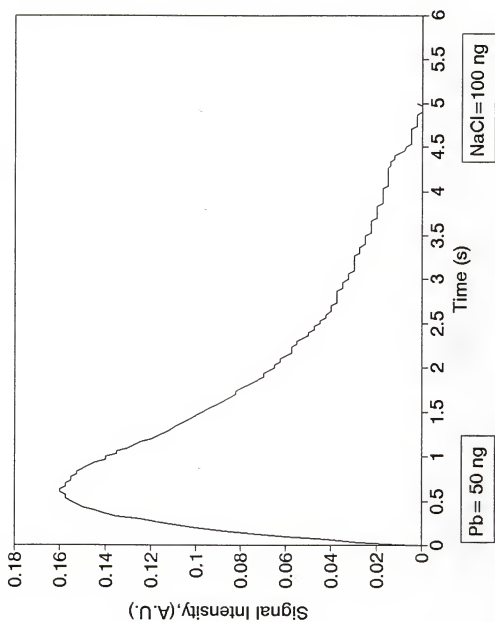


Figure 3.15. Temporal behavior of 50 ng of lead in presence of 0.5 μg of NaCl.

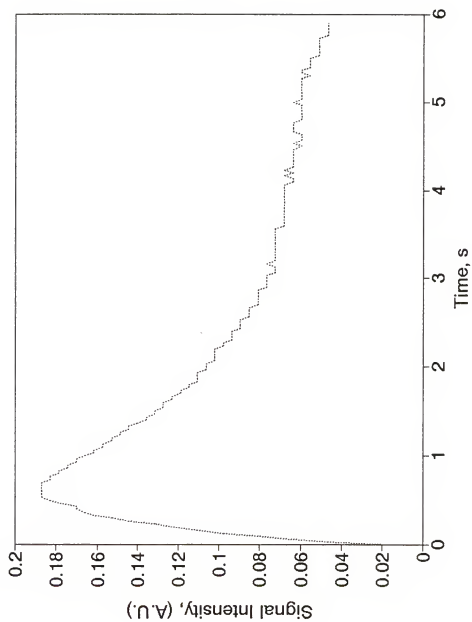


Figure 3.16. Temporal behavior of 50 ng of lead in presence of 5 μ g of NaCl.

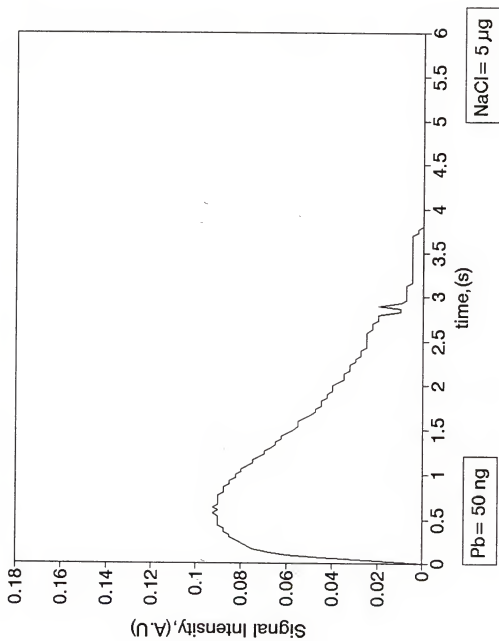


Figure 3.17. Temporal behavior of 50 ng of lead in presence of 10 μg of NaCl.

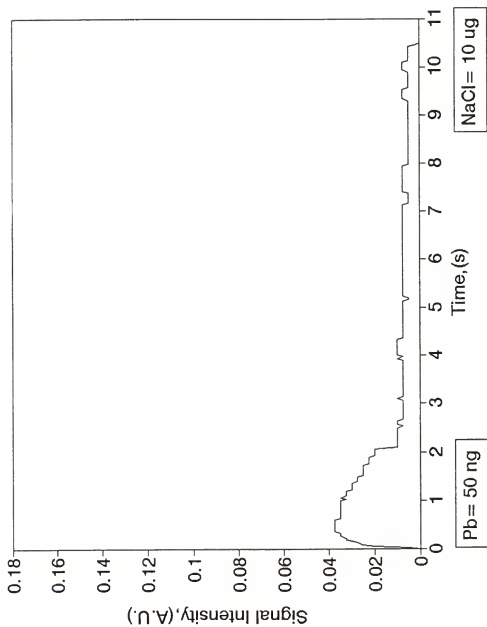
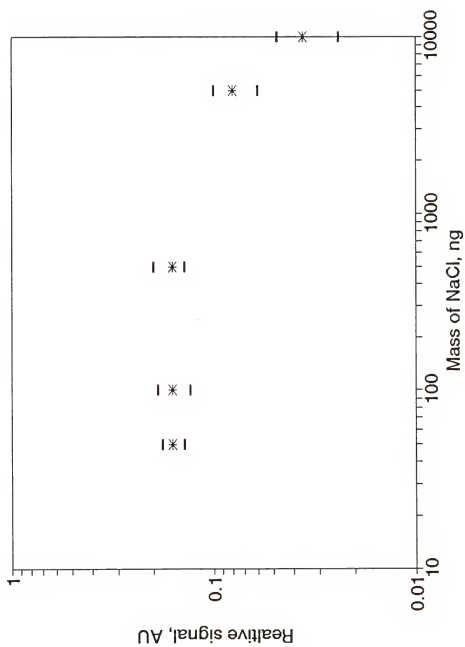


Figure 3.18. Log-log plot showing the effect of NaCl on the signal of 50 ng of lead.



determination of lead by atomic absorption spectroscopy using electrothermal vaporization (100,101). The use of nitric acid or ammonium nitrate to form volatile chlorides has succeeded in the elimination of the chloride interference (98). In this work, nitric acid was not used because of its chemical reactivity with the copper electrode, and therefore, was examined as a matrix modifier.

It was already established that 50 ng ($0.5\ \mu\text{L}$ 100 ppm Pb) of lead in the presence of 5000 ng ($0.5\ \mu\text{L}$ 10000 ppm NaCl) of sodium chloride produced a 50% decrease in the lead emission signal. Therefore, a solution that was 100 ppm in lead, 10000 ppm in sodium chloride, and 10000 ppm in ammonium nitrate, and another with the same concentration of lead and sodium chloride, but 20000 ppm in ammonium nitrate were prepared. Again, sample aliquots of $0.50\ \mu\text{L}$ were taken to run the experiments under the same operating conditions used in the matrix interference study. The measurements were performed for three different samples and in all of them the lead emission signal was completely quenched. These results suggest that the ammonium chloride did not inhibit the interference due to chlorides but actually increased the interference by perturbing the sputtering process. To account for this result, it was necessary to recall that the atomization process in the glow discharge with a cooled hollow electrode is not a thermal but an impingement process in which effective collisions between energetic species and analyte atoms cause the ejection of atoms from the cathode surface. Therefore, the more concomitant atoms surrounding the analyte atoms, the fewer analyte atoms are available to be ejected per unit of surface area per unit of time.

Measurement of Gallium

Application of the glow discharge-atomic emission system with wavelength modulation to determine gallium was also addressed. Taking into consideration the current use of gallium in the electronic industry, its determination at the trace and ultra-trace level in high purity materials is of major importance.

The 287.4 nm atomic line was selected for this element and the monochromator was calibrated using a hollow cathode lamp (Fisher Scientific). The same experimental operating conditions and procedure used with lead were applied to gallium. Different amounts of the analyte as the nitrate salt ranging from 25 ng to 400 ng were measured in triplicate. The discharge was initiated after setting the voltage at 1200 V which produced a current of 175 mA.

Figure 3.19 represents the calibration curve that resulted from plotting the peak area versus the mass of analyte. After applying the linear regression method, a slope of 0.97 was obtained. The datum for 400 ng was not included because it deviated considerably from linearity, most likely as a result of self-absorption. Figure 3.20 is a log-log plot of the calibration curve. It shows a slope equal to 1.0 which is an indication of the linearity of the curve over this range of masses. Using a statistical factor of three standard deviations and an average RMS noise of 8 nA obtained for ten different determinations a limit of detection equal to 300 pg was obtained.

Figure 3.19. Gallium calibration curve at 190 mA. ($P = 2$ torr, electrode depth = 8 mm).

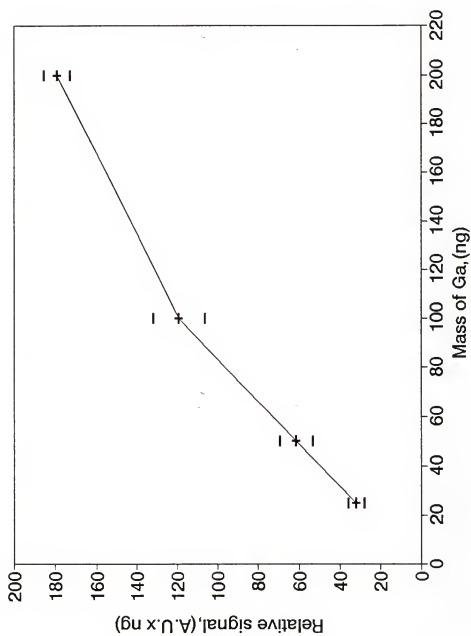
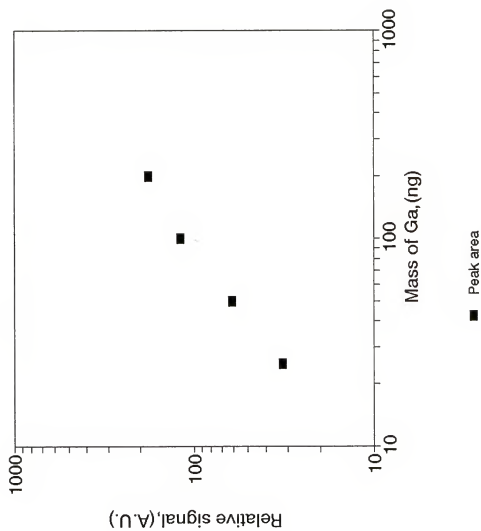


Figure 3.20. Log-log plot of gallium analytical calibration curve.



CHAPTER 4

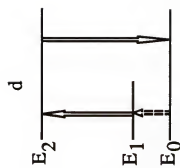
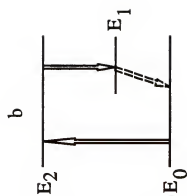
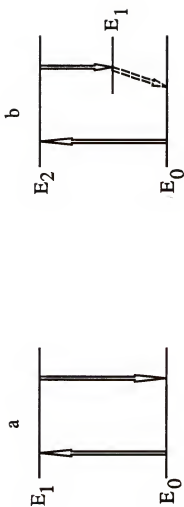
PRINCIPLES OF LASER EXCITED ATOMIC FLUORESCENCE SPECTROSCOPY

Atomic Fluorescence

Atomic fluorescence is a radiational deactivation process. To occur, it is necessary for an excitation of the atomic population by an external excitation source to take place (102). The emission of radiation may have the same wavelength as the exciting line. In this case, the fluorescence is called resonance (Figure 4.1a), in contrast with non-resonance fluorescence in which the wavelength of the emitting radiation is shifted. In this case, three energy levels of the atom are involved as shown in Figure 4.1b,c,d.

Taking into account the energy levels from which the fluorescence transition occurs, atomic fluorescence is classified as: direct line fluorescence if the upper energy level of the exciting line and the fluorescence produced are the same (Figure 4.1b), and stepwise line fluorescence when those two levels are different (Figure 4.1c,d). If the wavelength of the observed fluorescence is larger than that of the excitation source, the emission is called Stokes fluorescence; if the wavelength is shorter, the emission is called anti-Stokes fluorescence. In addition to this type of fluorescence, there also exists sensitized fluorescence. This type of radiation is

figure 4.1. Different types of fluorescence; a, resonance; b,c,d, non-resonant; b, direct line; c,d, stepwise.



produced when an atom which has been excited by an external source, and this excited atom transfers its excitation energy to the analyte atom which then undergoes radiative deactivation, giving rise to a step-wise line fluorescence.

Excited atoms have a finite probability indicated by the Einstein coefficient, A_{ji} , to undergo a deactivation process. Also, there is a finite lifetime of the excited atoms, and during this time, the excited atom can lose part of its energy by non-radiative processes, for instance, by collisional interaction with others species present in the atom cell (103). As a result, a decreased fluorescence signal will be observed, and this phenomenon is called a quenching process. The fluorescence quantum efficiency or fluorescence quantum yield, Y_f , is a measure of the fraction of absorbed photons that are emitted as fluorescence photons (104). This parameter is given by the equation

$$Y_f = A_{ji} / (A_{ji} + \Sigma k_j) \quad (4.1)$$

where A_{ji} = rate constant for spontaneous emission, s^{-1} .

Σk_j = sum of the rate constants for all the deactivation processes, s^{-1} .

Because the radiative lifetime of the upper level is equal to

$$\tau_s = A_{ji}^{-1} \quad (4.2)$$

and its observed lifetime is expressed as

$$\tau_o = (A_{ji} + k_j)^{-1} \quad (4.3)$$

and equation 4.1 can also be written as

$$Y_f = \tau_o / \tau_s \quad (4.4)$$

If a spectral continuum source (e.g., a source spectrally much broader than the atomic absorption line) is used to produce the excitation process, the total fluorescence radiant power Φ'_F , in W, produced can be calculated from

$$(\Phi'_F)' = 8.82 \times 10^{-13} \lambda_m^2 (\Phi_{\lambda_m})_0 Y n_i f_{ij} l \quad (4.5)$$

where

λ_m = wavelength at the line center of the source, nm,

$(\Phi_{\lambda_m})_0$ = source spectral radiant power at the line center, W nm⁻¹,

Y = fluorescence quantum efficiency (if the emitted $h\nu_F$, and absorbed, $h\nu_A$ photon energy are not equal, the fluorescence power efficiency, which is equation 4.1 x $h\nu_F/h\nu_A$ must be used).

n_i = concentration, cm⁻³,

f_{ij} = absorption oscillator strength, dimensionless,

l = pathlength, cm.

According to equation (4.5), the fluorescence radiant power is directly proportional to the analyte concentration and to the source radiant power. For high atomic concentrations, the system is no longer optically thin, and the total fluorescence radiant power, (Φ'_F) , is proportional to $(n_i)^{1/2}$.

When a spectral line source of wavelength, λ_m , is used to produce the excitation under optically thin conditions,

$$\Phi_F = \Phi_0 \alpha_i Y \quad (4.6)$$

$$(\Phi'_F)_{nl \rightarrow 0} = 8.82 \times 10^{-13} \lambda_m^2 \Phi_0 Y n_i f_{ij} l / \Delta\lambda_{\text{eff}} \quad (4.7)$$

where Φ_0 = incident source radiant power, W.

Again, the fluorescence signal is directly proportional to the analyte concentration and to the intensity of the source. At high analyte concentration, α_i in equation 4.6 approaches unity and

$$\Phi'_F = \Phi_o Y \quad (4.8)$$

Therefore, the fluorescence signal becomes independent of the atomic population in the ground state because all the radiation from the source is absorbed by the analyte atoms. In the presence of self-absorption, the fluorescence signal is given by

$$\Phi_f = \Phi'_F f_s \quad (4.9)$$

where

f_s = fraction of fluorescent photons which is not reabsorbed

Φ'_F = fluorescence radiant power produced in a volume V

Φ_F = observed fluorescence radiant power

Taking into consideration the above relationships between the fluorescence radiant power and the analyte population, the variation of the fluorescence signal with analyte concentration n_i is linear at lower concentrations for either continuum or a line source excitation. This characteristic makes this procedure especially useful for trace and ultra-trace analysis. At high analyte concentrations, the fluorescence signal is proportional to the square root or is independent of the atomic population depending if a continuum or a line source is used in the experiment. In the presence of self-absorption, a plateau is reached at high n_i values when using a continuum source and a negative log-log slope is reached when using a line source ($\Phi_F \propto 1/(n_i)^{1/2}$).

When a laser is used as the excitation source, the absorption coefficient, k , is not independent of the source radiant power as it is assumed for other line sources such as the hollow cathode lamps. A complete discussion of the radiance fluorescence expressions with laser excitation for a two or three level system is given by Omenetto and Winefordner (105). According to them, the fluorescence radiance for a basic two-level system using a low irradiance source is given by

$$B_F = (1/4\pi)Y_{21}E_\nu(\nu_{12}) \int k(\nu)\partial\nu \quad (4.10)$$

where

B_F = fluorescence radiance, $\text{erg s}^{-1}\text{cm}^{-2}\text{sr}^{-1}$,

4π = number of steradians in a sphere, sr,

E_ν = spectral irradiance of exciting radiation at absorption line, ν_{12} , W,

$\int^\infty k(\nu)\partial\nu$ = integrated absorption coefficient over absorption line, m^{-1}Hz .

According to equation (4.10) the fluorescence radiance depends linearly upon the source spectral irradiance and the quantum efficiency of the transition. Under this condition, no saturation is achieved.

For a high excitation irradiance

$$B_F = (1/4\pi)h\nu A_{21}n_T[g_u/(g_u + g_l)] \quad (4.11)$$

where

g_l, g_u = statistical weights of the lower and upper level, respectively.

Equation (4.11) shows that, if a high irradiance source (like a laser) is used as the excitation source, the atomic fluorescence irradiance does not depend on either the source irradiance, or the quantum efficiency, (Y), of the fluorescence

process. When this situation occurs, optical saturation is achieved. To work under conditions of optical saturation opens the possibility of determining absolute concentrations if the fluorescence signal is measured in absolute units by using a calibrated spectrometer.

Winefordner and Vickers (106) in 1964 proposed and demonstrated the utilization of atomic fluorescence in spectrochemical analysis. In their initial work, a flame was used as the atomizer. Besides the discussion of the theoretical and instrumental aspects of the technique, they also reported the advantages and disadvantages of the new approach for elemental analysis.

The basic instrumentation for atomic fluorescence spectroscopy (AFS) consists of: 1) an excitation source, 2) the atom cell, 3) a monochromator, 4) a detector, and 5) a readout system. Initially, a flame was the atom cell, but later electrothermal atomizers (107), inductively coupled plasmas (108), and glow discharges (102) have been utilized as atom reservoirs for AFS. The use of high intensity sources in AFS enhances the sensitivity of the procedure. For this reason, tunable dye lasers deserve especial attention. The use of a laser as a line source for atomic fluorescence spectroscopy opened a novel and important area of research called Laser Excited Atomic Fluorescence Spectroscopy (LEAFS) which will be treated later in this chapter.

Basic Principles of Lasers

According to quantum theory, a system formed by atoms, ions, or molecules has a series of well defined, discrete levels of energy. In the absence of any external

perturbation, the species of the system tend to be in the lowest energy level or ground state. These species can be selectively promoted to a higher energy level by absorption of radiation of photons of energy equal to the difference between the final and initial state of the species. Particles in the excited state are unstable, they rapidly (normally in nanoseconds) give up the previously absorbed energy by a process called emission. Spontaneous emission is said to occur when the deactivation process occurs isotropically. The directional, coherent enhancement by an external source is called stimulated emission. In this latter case, the radiation used to excite the system must have a frequency equal to the frequency of the emitted radiation. Stimulated emission is characterized by having the same direction of the excitation radiation producing an amplification of the intensity of the emitted radiation (109).

When a plane electromagnetic wave propagates along a certain axis and interacts with an atomic population, atomic absorption as well as stimulated emission occur simultaneously (110). The photon flux variation for a distance, dx , of the system is given by

$$(dJ/dx) = \sigma J(N_2 - N_1) \quad (4.10)$$

where σ = absorption cross section, cm^2

J = photon flux, $\text{cm}^{-2}\text{s}^{-1}$

N_2 = atomic population in level 2, dimensionless

N_1 = atomic population in level 1, dimensionless

x = distance, cm

If $N_2 - N_1 > 0$, then the system is said to be an absorber, if the variation of the flux with the distance is positive, a population inversion is obtained and the system behaves like an amplifier. If the wavelength of the transition is in the optical range (UV to IR), the system is called a LASER which stand for "light amplification by stimulated emission of radiation".

Basically a LASER is formed by three parts as seen in Figure 4.2, 1) the active medium, where the amplification occurs; 2) the energy pump which produces the population inversion by pumping the necessary energy to the active medium, and 3) the optical resonator composed of two parallel mirrors, one of which is designed to reflect approximately 100% of the stimulated emission. The other mirror partially reflects the light and is used as the output of the laser system.

Properties of the Lasers

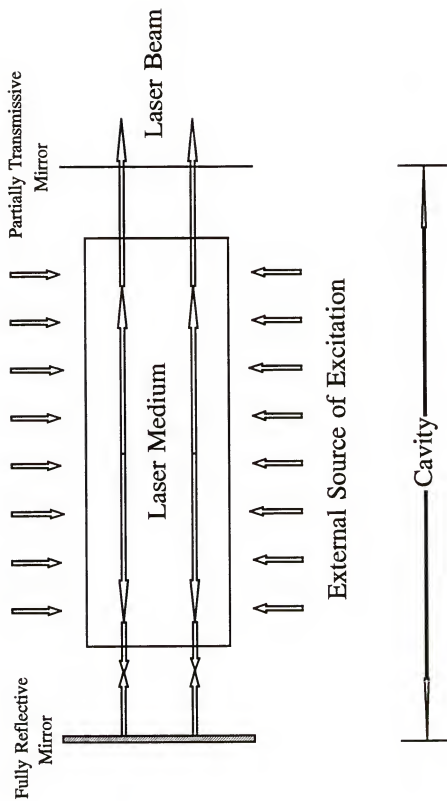
Laser emission is characterized by the following properties: 1) directionality, 2) high irradiance, 3) monochromaticity, and 4) coherence.

Directionality

Because of the configuration of the resonant cavity which determines the path of the beam, the laser radiation is confined to a narrow cone of angles. From diffraction theory a spatially coherent beam with aperture D has a limited intrinsic divergency α_D given by

$$\alpha_D = \lambda/D \quad (4.11)$$

figure 4.2



where

λ = wavelength of the radiation, nm

A typical figure for the angle of beam divergence is 1 milliradian and the beam diameter is around 1 millimeter. This laser property is applied in optical alignment (e.g. monochromators) and in monitoring of atmospheric pollutant gases.

High Irradiance

Lasers are characterized by having an extremely high intensity when compared with other conventional light sources like hollow cathode lamps. This property is the result of the very well defined directionality and divergence of the laser beam. For example, a moderate power argon laser emits 10 W at a wavelength of 488 nm (111). Assuming a cross sectional area of 1 mm^2 , the laser irradiance would be 10^7 Wm^{-2} .

Monochromaticity

The stimulated emission in a laser system occurs between resonant transitions. This results in a radiation characterized by having a narrow range of frequencies. Monochromaticity is mainly the product of the higher gain of the optical amplifier which enhances the central frequency of the active transition. Also, the resonant cavity formed by the mirrors selectively enhances oscillations among resonant frequencies of the cavity. This is achieved by making the cavity length equal to an integer number n of half-wavelengths.

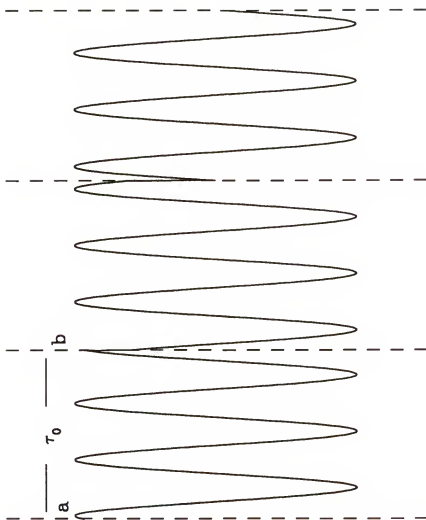
Coherence

Coherence is the laser property which most clearly distinguishes this radiation from other kinds of radiation. Coherence indicates the uniform correlation between the phases of different photons. It is classified into spatial and temporal coherence. Spatial coherence occurs when any two points a and b of a wave with electric fields E_a and E_b , have a phase difference equal to zero at any time. By definition, the phase difference at E_a and E_b at time equal to zero is zero (Figure 4.3). Temporal coherence occurs if a given point of the wave, at time t_1 and $t_1 + dt$, for a given time delay dt , the phase difference remains constant for any time.

Types of Pulsed Lasers

Based on the characteristics of the active medium, pulsed lasers may be classified in four categories: gas, solid state, semiconductors, and liquid lasers. Examples of pulsed lasers are the Nd-YAG, excimer, nitrogen, and copper vapor laser (CVL). A laser can be pumped optically by means of flashlamps as in the case of dye and Nd-YAG lasers. The pumping can also be achieved by means of electrical discharges like in the case of the CVL or by applying an electrical potential to the active medium like in the diode lasers. If the rate of pumping is not superior to the rate of decay from the upper laser level, population inversion is not sustained and the laser works only in the pulsed mode. The pulse duration depends on the kinetics of the stimulated emission process.

Figure 4.3. Spatial and temporal coherence in a laser (see text for explanation).



The nitrogen laser is an example of a molecular gas laser; it is excited by a high voltage electrical discharge to produce high intensity peak power in the UV (see Table 4.1). Nitrogen lasers have been used to pump dye lasers in LEAFS.

Among the solid lasers, the neodymium laser uses Nd^{+3} as the active medium. If the host crystal for the neodymium ions is a yttrium aluminum garnet ($\text{Y}_3\text{Al}_5\text{O}_{12}$) the laser is called Nd-YAG laser. Amorphous glass is also utilized as the host crystal and in this case the laser is called Nd-glass laser. The principal emission line produced by the two types of Nd^{+3} lasers is $1.064\text{ }\mu\text{m}$ (near IR). The Nd-YAG laser can be utilized in the pulsed and in the continuous mode but the Nd-glass works better in the pulsed mode because the glass does not have the appropriate thermal conductivity to operate efficiently in the continuous mode.

In semiconductor lasers, the active medium is a semiconductor material. A population inversion is obtained between the bottom of the conducting band and the top of the valence band of a p-n junction. The bandwidth of diode lasers in the near infrared is adequate to perform high resolution spectroscopy. They are tunable over short wavelength ranges. Tunability is achieved by changing the current or temperature of the semiconductor. Gallium arsenide salts are commonly used as the active medium to produce lasers in the red and near infrared regions of the spectrum. Liquid lasers or dye lasers use a fluorescent organic dye in solution as the active medium. They have to be pumped, and this can be done with a flash lamp or with another laser. The main advantage of these lasers is that they are tunable over a wide range of wavelengths, typically 20 to 100 nm. By using different dyes, lasing

Table 4.1 Types of Pulsed Lasers (109)

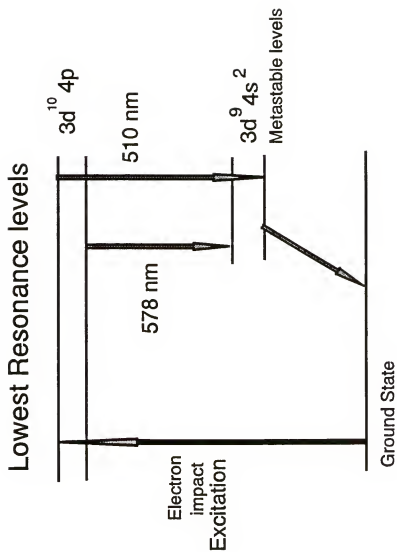
Type	Name	λ , nm	Bandwith, nm	Power, W	Repetition rate
Gas	CVL	520, 510	0.01	20	5 to 7 KHz
	N ₂	337.1	0.1	1	1-200 Hz
Solid	Nd-YAG	1060	10	10	1-200 Hz
	Semiconductor (InGaAsP)	1100-1600	0.1	0.050	1000 Hz
Dye	Liquid	UV-VIS	0.1	0.050	1 Hz to 7 KHz

action can be obtained from approximately 200 nm to 1000 nm. Many polyatomic molecules with large electron delocalizations are used as active mediums for dye lasers. Although the efficiency of dye lasers are low, they are very useful in analytical applications because of the narrow bandwidth and short pulses that can be obtained.

The Copper Vapor Laser

Part of the studies of this dissertation were performed with a copper vapor laser (CVL). The CVL is classified as a gas or metal vapor laser. The active medium in this system is vaporized copper which is obtained from small pieces of the metal placed inside an alumina tube. To obtain the copper vapor, the tube is heated to about 1500°C by means of an electrical discharge. At this temperature the copper vapor pressure is about 0.1 torr. This copper vapor acts as the active medium of the system. The tube is filled with neon at working pressures of 20 to 40 torr as the buffer gas. Copper atoms are excited according to the scheme illustrated in Figure 4.4 by a pulsed high voltage discharge. When in operation, copper atoms fill the discharge tube. Since the end windows must be kept below the plasma tube temperature, axial temperature gradients contribute to diffusion of copper atoms toward the end of the cavity. However, due to the lower atomic weight and density of the buffer gas (Ne), the copper loss rate is only of the order of 10 mg per hour. Therefore, the CVL can be operated for several months before additional copper must be placed within the plasma tube. The duration of the pulse is about 40 ns, and the energy produced is in the millijoule range. The repetition rate can be varied

Figure 4.4. Copper atomic transitions in the copper vapor laser.



between 5 and 10 kHz. In addition to its high repetition rate, another important feature of this laser is its high average power, which is around 20 W. The main disadvantage of the CVL is its long warm up time and relatively low peak power compared to other pulsed lasers. Normally, 1 to 2 hours are required before the laser is ready to pump a dye laser.

According to Alkemade (67), the use of a high repetition rate laser as an excitation source in atomic fluorescence spectroscopy enhances the atomic probing efficiency and therefore, an increase in the sensitivity should be achieved. Therefore, the use of the CVL in the atomic fluorescence studies was very important because a transitory atomic population (a few seconds of duration) was obtained. In this case the sensitivity of the determination depends very much of the probing efficiency of the excitation source.

Laser Excited Atomic Fluorescence Spectroscopy

This technique is based on the utilization of a dye laser as the excitation source for atomic fluorescence. The most important advantage of using a laser source is based on its high spectral irradiance and spectral selectivity. As was established before, the intensity of the fluorescence signal depends directly on the irradiance of the source. Therefore, dye lasers are more powerful line sources than hollow cathode lamps (HCL). Excimer, Nd-YAG, nitrogen, argon and copper vapor lasers have been used to pump dye lasers. Except for the CVL, the others have low repetition rates (see Table 4.1). Adequate measurement, precision, and high

sensitivity are achieved with lasers of repetition rates of about 50 Hz when flames and plasmas are the atom reservoir. However, this frequency is not adequate for electrothermal atomizers and glow discharges because their signals are transients and therefore need to be probed at higher rates. In this case, the CVL has been shown to be an excellent source as can be confirmed by the study of Vera et al. (112).

A more complete and detailed explanation about the instrumentation as well as the application of LEAFS will be given in the next chapter.

CHAPTER 5

STUDY OF THE SPUTTERING PROCESS OF MICROSAMPLES IN A GLOW DISCHARGE WITH LASER EXCITED ATOMIC FLUORESCENCE SPECTROSCOPY

Introduction

The utilization of LEAFS is increasing for trace and ultra-trace analysis of metals. This method, like many others, involves the atomization of the sample which can be a solid or a liquid. Most of the known atomizers have been evaluated for LEAFS. These include flames (66,113), electrothermal atomizers (50,57,58,114-117), inductively coupled plasmas (53,118-119) and glow discharges (59,61,64-65,80).

For atomic fluorescence, the GD has been operated in the pulsed mode and the fluorescence signal has been detected when the GD is off where the background noise produced by the atomizer is at minimum (119). When GDs are compared with atmospheric pressure atomizers like flames and plasmas, they offer the advantages of producing narrow spectral atomic lines and a reduced quenching environment and are therefore easier to saturate the atomic absorption transition making the GDs perfect atom reservoirs for LEAFS. This was demonstrated by Smith et al. (60) using a commercial hollow cathode lamp as the atom cell to measure the atomic

fluorescence of lead after excitation with a CVL pumped dye laser. They found an LOD of 1.8 ag within the laser volume and extrapolated to a single laser pulse.

The utilization of GD-LEAFS for the analysis of solid materials has been reported by Grazhulene and coworkers (120) who determined lead in microelectronic samples and found an LOD of 40 ng/g. In another work, Travis et al. (63) reported the determination of sodium and iron in conducting samples with an LOD on the order of part per billions.

Measurements of Metals in Solutions by Glow Discharge-Laser Excited Atomic Fluorescence Spectroscopy

Smith et al. (59) used a nitrogen pumped dye laser system as an excitation source for a 20 Hz pulsed, direct current GD. In their work, 5 μL of lead solution was placed in a graphite hollow electrode and dried with an IR lamp. An LOD of 20 pg was obtained. In another other study, Patel and Winefordner, (80) using the same system employed by Smith et al. (59), reported the determination of indium in aqueous solutions. Samples volumes of 10 μL were used and an LOD of 8 ng was obtained. Liquid samples were also analyzed by Glick et al. (65). In the study of Glick et al., a XeCl excimer laser pumped dye laser was used as the excitation source for samples with volumes of 2 μL . Experimental LODs of 0.5 and 20 pg were obtained for lead and iridium, respectively. The determination of cobalt and nickel using GD-LEAFS was also reported by Lunyov and Oshemkov (64) using dried residues of liquids. LODs of 15 ppt for Co and 5 ppb for Ni were obtained. Finally, Womack et al. (61), using the same approach reported by Glick et al. (65) but with

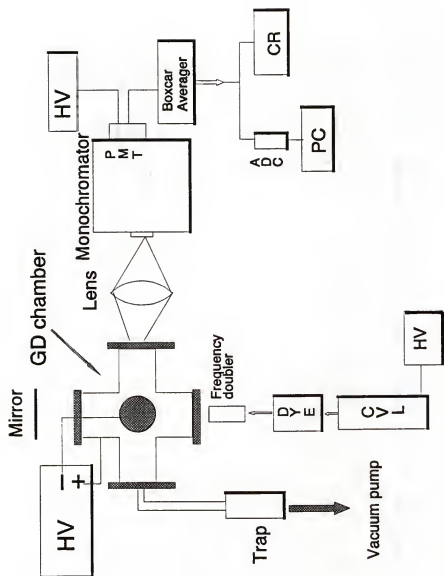
a CVL pumped dye laser as the excitation source, obtained an LOD of 15 pg for liquid samples using volumes on the order of 10 μL .

The objective of the present work was to study the sputtering process in a low pressure GD with argon as the filler gas and a hot planar copper electrode as the sample holder using LEAFS. The system was optimized to follow the temporal behavior of the analyte which was sputtered from the cathode within a few seconds. The performance of the atomizer in the continuous and pulsed modes was examined by mapping the fluorescence and background response at different positions in between the electrodes and below the anode. Fluorescence signals were taken at 90° from the laser path to reduce any contribution to the signal from laser scattering. After selecting the best GD operating conditions as well as the best observation zone, the system sensitivity was evaluated for lead. As in the GD-AES work already presented in chapter three, the effect of sodium chloride as a matrix interference also was studied.

Instrumentation

Figure 5.1 shows the experimental geometry. Direct observation of the fluorescence at 90° without the use of a pierced mirror enhances light collection. The copper vapor laser (CVL 251, Metalaser Technologies, Pleasanton, CA; 20 W average power, 6 kHz repetition rate, pulse width 20 ns) was used to pump a dye laser (Molelectron DL-II, Rhodamine 6G) whose output was then frequency doubled

Figure 5.1. Glow discharge-Atomic Fluorescence system.

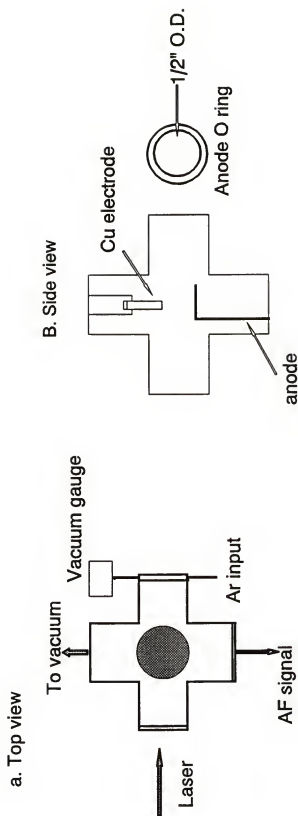


(Model 390 Frequency Doubler, Spectra Physics, KPD crystal) and directed unfocused into the GD plasma. The dye laser and doubling crystal were tuned to the 283.3 nm lead transition by placing enough lead salt on the planar electrode to produce a constant signal.

A plane mirror was used to fold the laser light back on itself, and this resulted in a near doubling of the fluorescence signal. The fluorescence flux was collected by a plano-convex lens for collimating and then focused onto the entrance slit of the monochromator (Minimate, $f/4$, 10 nm spectral bandpass, Spex Industries, Inc.) by a matching plano-convex lens. The monochromator was tuned to the 405.7 nm lead transition. The fluorescence was detected by a photomultiplier tube, (PMT, Hamamatsu type R1547) operated with an anode to cathode voltage of -900 V. A Princeton Applied Research model 181 current sensitive preamplifier was used as a current to voltage converter for the output from the PMT. This signal was then passed into the boxcar integrator/gated detector (SR250, Stanford Research Systems). The gate used was 1.5 μ s with a delay of 100 ns. One thousand pulses were averaged. The boxcar output was displayed on a strip chart recorder (Bausch and Lomb D5117-5AD) and also was sampled at a rate of 1 kHz by an analog-to-digital converter (SR 245, Stanford Research System, Palo Alto, CA) for storage on a minicomputer.

Figure 5.2 shows the glow discharge assembly used in the fluorescence work. The cathode was a 1.0 in. long by 1/4 in. diameter copper rod threaded on one end with a 1/4-20 thread. This removable section was threaded into a correspondingly

Figure 5.2 Glow discharge assembly for the fluorescence studies.



tapped 1/4-20 hole bored into the end of 1.0e in copper feed through (MC-600, MDC Vacuum Products Corp.). The feed through was insulated with a quartz tube. A ceramic covered all except 0.1 in. of the removable electrode when the electrode was screwed into position. The ceramic sleeve was held in place by a teflon washer.

The glow discharge was maintained in a vacuum chamber identical to the one used previously in the atomic emission experiments. The six ports of the glow discharge assembly were used to connect the vacuum, hold the cathode, hold the anode, input argon and monitor the pressure, allow the input of the excitation laser beam, and to monitor fluorescence. The feed-through holding the cathode was held in place by gravity and an o-ring provided the vacuum seal. The negative lead of the power supply was attached to the cathode. The anode was a 1/2 in. diameter stainless steel ring silver soldered to a 1/8 in. stainless steel post that was electrically insulated from the vacuum chamber by means of a ceramic tube. It was positioned 4.5 mm from the cathode surface when the cathode was placed in position. Pressures were monitored by a mechanical gauge (Speedivac Type CG3, Edwards High Vacuum Corp.). Optimum operating voltages were in the 400-500 V range while currents were in the 10-30 mA range. The voltage and current could not be independently controlled. Optimum experimental conditions were determined as those given the best signal to noise ratio while not causing arcing to occur.

The glow discharge also was operated in a pulsed mode using a circuit described by Glick et al. (65). The pulse to the glow discharge was triggered by the laser pulse. The optimum pulse length was determined to be 50 μ s which was

initiated 120 μs after the laser pulse. The discharge would reach a maximum emission intensity of 63 μs after the start of the pulse and would decay to a minimum 100 μs after the end of the pulse from the power supply.

Standard solutions (0.1 $\mu\text{g/mL}$ -100 $\mu\text{g/mL}$) were pipetted onto the surface of the copper electrode by the same micropipet used in the emission work. Aliquots (100-1300 nL) were deposited on the copper electrode and were heated by means of an infrared lamp until dried (1-3 min) prior to screwing the electrode into the feed through for introduction into the vacuum system. The chamber was evacuated and then filled with argon to the desired pressure. The average time to perform an analysis was five minutes. The data were manipulated by use of software which permitted measuring of the peak height or peak area and calculations of statistical parameters.

Results and Discussions

Figure 5.3 shows the variation of the fluorescence signal with the pressure of fill gas. On the basis of these results, 5 torr was chosen as the operating pressure for the rest of this work. To select the GD working current, fluorescence was observed at different currents between 5 mA and 40 mA. Above 30 mA the plasma stability started to decrease producing spurious signals and around 40 mA the plasma started to arc. Figure 5.4 shows the fluorescence signal dependence upon current for a stable GD. Taking into account this information, the GD was operated at 25 mA in the fluorescence studies.

Figure 5.3. Variation of lead fluorescence signal with pressure ($I = 20$ mA).

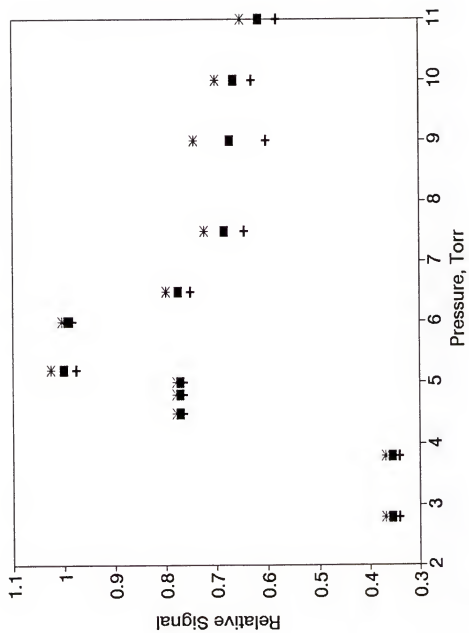
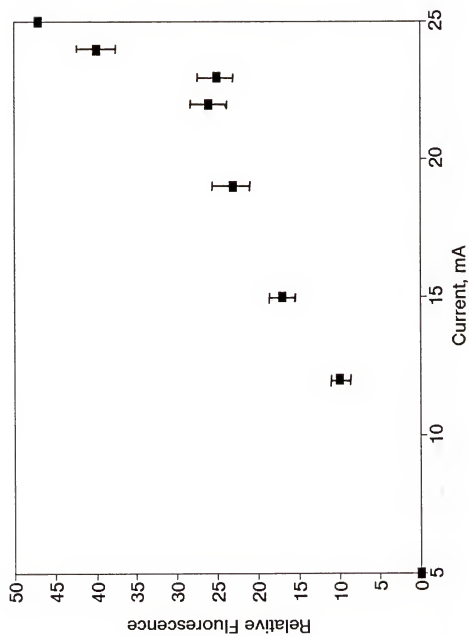


Figure 5.4 Variation of lead fluorescence signal with current.



Figures 5.5 and 5.6 show the vertical profiles (distance from cathode) of fluorescence and background emission intensities for the pulsed and non-pulsed GD, respectively. These signals were observed between A and C as shown in Figure 5.7. The pulsed GD mode was shown to be of little value due to the high pulse frequency of the GD which was controlled by the copper vapor laser. Within this short time regime, it was found that at the current used, the plasma did not have enough time to return to a completely dark state. Therefore, the background emission could not be completely discriminated against by the boxcar detection system. This finding agrees with the study done by Ferreira et al. (37) about the role of metastable atoms in the afterglow plasma of a low pressure discharge. Ferreira found that argon metastable absorption (spectral lines terminating on metastables levels) increased to a maximum approximately 100-150 μs after termination of the current, and the continuum emission was still observed 200 μs after the GD (using a copper electrode) was turned off. The background vertical profile (Figure 5.5 and 5.6) determined in the present study showed that it is advantageous to measure the fluorescence signal below the anode where the background emission is essentially zero. The decrease of the fluorescence signal at distances approaching 0.45 cm from the cathode is a result of the anode blocking the optical axis. The remarkable feature is the uniform atom distribution seen well past the anode (Figure 5.5) and the negligible background emission (Figure 5.6). The limiting distance turned out to be the edge of the viewing port at 1.8 cm from the cathode surface. These measurements were performed with an electrode encrusted with a lead salt.

Figure 5.5 Vertical profiles of lead fluorescence in a pulsed and non-pulsed glow discharge.

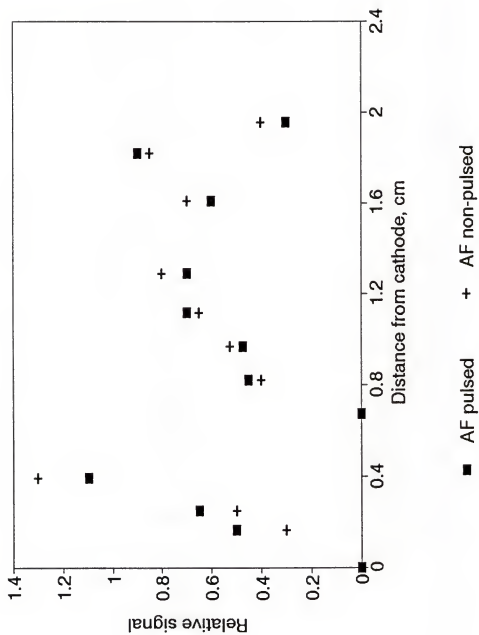


Figure 5.6. Vertical profiles of background emission signal in a pulsed and non-pulsed glow discharge.

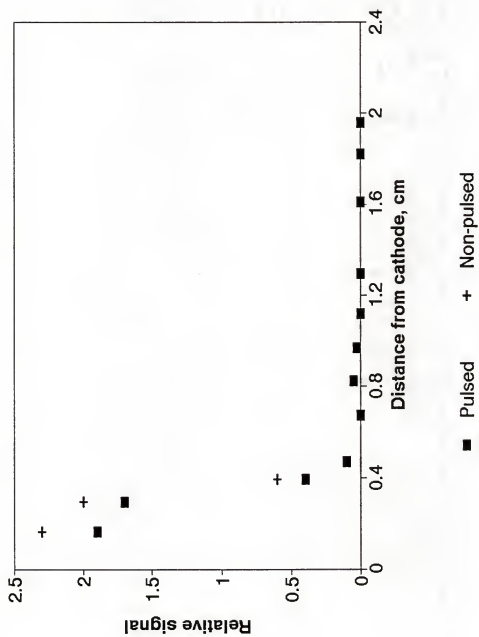
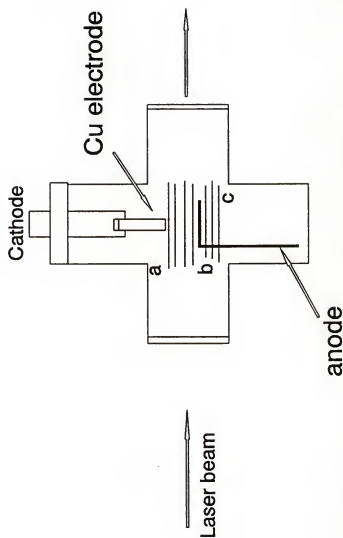


Figure 5.7. Glow discharge observation zone above and below the anode.



Measurements taken between a and b, and b and c.
Lines represent excitation zone.

The effect of the sample volume on the fluorescence response also was considered. Here, volumes of different concentrations of lead solution all containing 1 ng of lead were taken and measured in triplicate. The results using peak height and peak area are presented in Figure 5.8 and 5.9. Sample volumes greater than 200 nL using peak height gave better reproducibility than measuring peak area. For volumes of 200 nL or lower, errors in pipetting strongly affected the measurement of the signal. To avoid any effect on the sputtering process that may be a result of the use of different volumes, the same volume (0.5 μL) of different concentrations were utilized to evaluate the analytical figures of merit of the system.

Figure 5.10 shows the temporal profile of the atom cloud for 1 ng of lead. The maximum is reached within 1 s while the decay back to the background takes up to 3 s. The background signal lies above the dark current due to fluorescence of lead impurity within the copper electrode. When the laser beam was blocked while the discharge was on, the signal did, in fact, return to the equivalent of the dark current.

Figure 5.11 shows a log-log analytical calibration curve using peak height of the fluorescence signal versus lead mass. The slope of the curve was 1.12. The limit of detection using 3σ as the statistical factor was calculated to be 2 pg. Although the linear dynamic range is only of the order of 2-3 orders of magnitude, this value is acceptable for trace and ultra-trace analysis where the amount of analyte is usually of the order of a few nanograms or picograms and in this range the calibration curve is reasonably linear.

Figure 5.8. Plot of peak height versus volume used for 1 ng of lead.

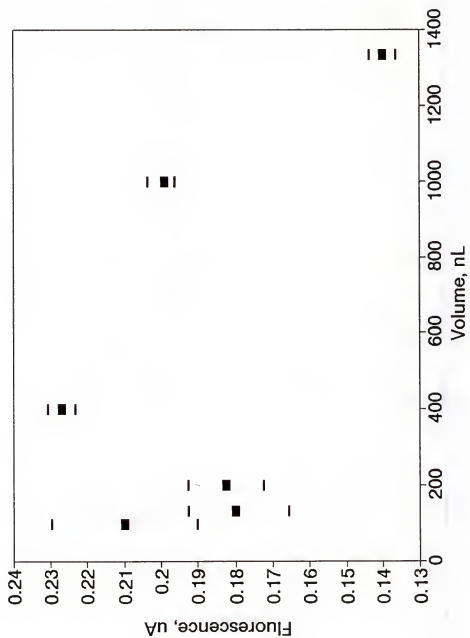


Figure 5.9. Plot of peak area versus volume used for 1 ng of lead.

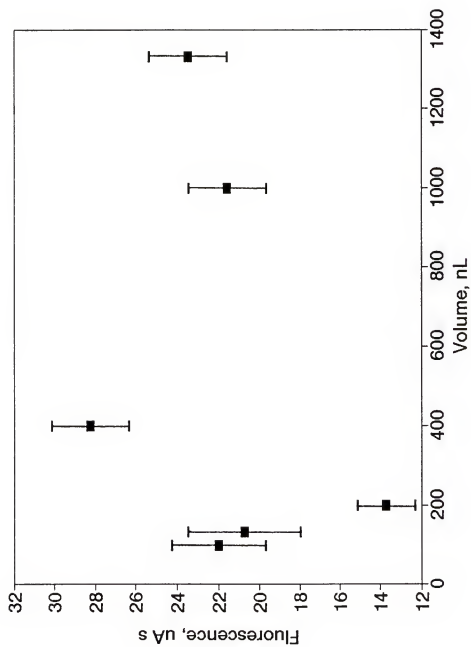


Figure 5.10. Lead fluorescence temporal profile for 1 ng of analyte at 25 mA.

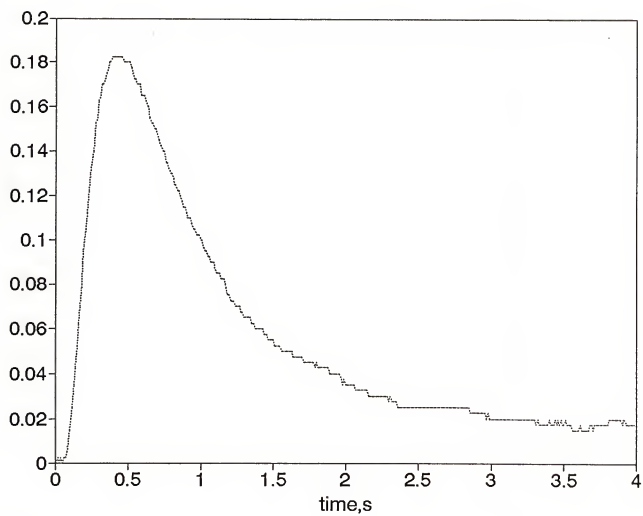
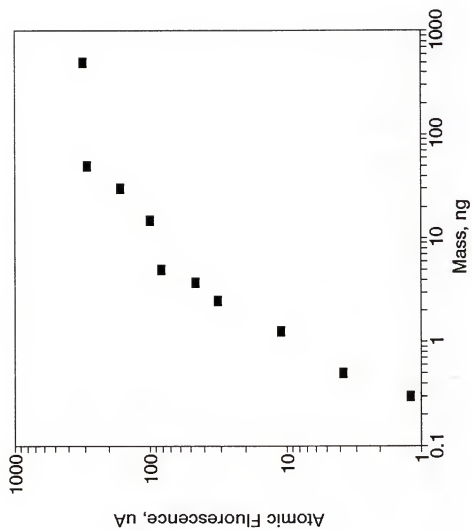


Figure 5.11. Log-log plot of the lead analytical calibration curve using LEAFS.



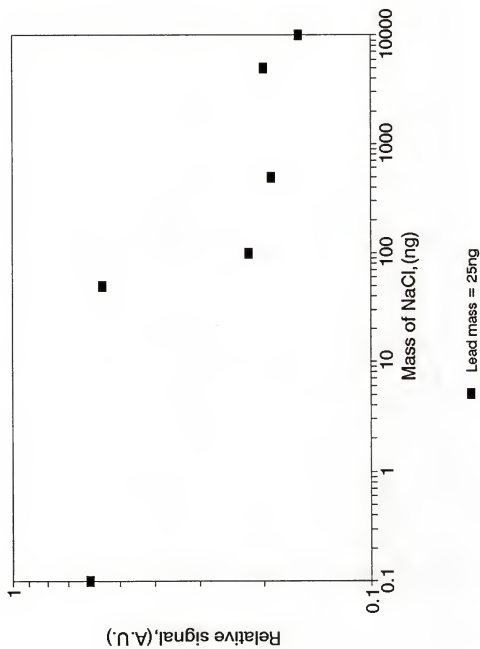
One important feature of the GD system is that no memory effects were observed from one analysis to the next. In addition, the performance of the atomizer was not affected by the continuous use of the same copper electrode through all this work in which a large number of measurements were carried out.

Study of the Matrix Interference

As was already seen in Chapter 3, the lead emission signal was also significantly quenched when the analyte was mixed with appreciable amounts of sodium chloride. From that study, no information about the lead ground state population could be obtained, and, therefore, it is not possible to deduce any conclusion about which process (sputtering rate or excitation process) in the GD is being affected by the matrix. Because atomic fluorescence is produced by an excitation process which involves the atom ground state population, the effect of sodium chloride on the lead fluorescence signal was studied.

Figure 5.12 shows the effect of several different amounts of sodium chloride on 25 ng of lead. From Figure 5.12, it seems that the ejection of the analyte from the surface is affected by the NaCl. A factor which should be considered is the change in the analyte chemical composition when lead in the form of nitrate is mixed with sodium chloride in such a way that the molar ratio NaCl:Pb is greater than unity. Here, the deposited film of sample on the cathode is basically lead chloride which may have different sputtering characteristics than lead nitrate. Also, the

Figure 5.12. Effect of sodium chloride on the lead fluorescence signal.



possibility of an increase in the ejection of molecular species or clusters of the analyte should not be disregarded. In this case, the analyte is being removed from the electrode in a form other than as free atoms and is therefore not detected.

Atomic Fluorescence Determination of Gallium

Gallium, which was studied by use of atomic emission, has the possibility of being studied by the use of atomic fluorescence with the copper vapor-dye laser system as one of its fluorescence schemes has an excitation wavelength of 287.4 nm. The fluorescence from this excitation is at 294.4 nm. The closeness of wavelengths (less than 10 nm) of the excitation and fluorescence lines presents difficulties, however, as laser scatter can become a problem. This is not seen with Pb where the excitation and fluorescence wavelengths are 283.3 and 405.7 nm, respectively.

There are three ways to try to circumvent this problem. The first is to make the laser probe distance from the cathode and anode large to reduce and/or eliminate laser scatter. Unlike Pb in which this could readily be accomplished, the Ga signal falls off dramatically with increasing distance from the cathode. Thus it is necessary to look as close to the anode as possible to achieve a large signal. Laser scatter will become the predominate noise source and will limit the lower end of the concentration range that can be studied and thus lead to a poorer limit of detection and limit the linear dynamic range.

The second method is to use narrower slits, thus reducing the spectral bandpass of the monochromator. This increase in resolution, however, reduces throughput and thus reduces the signal to a degree that is unacceptable.

The third method of reducing laser scatter would be to employ a filter between the discharge and the monochromator that would selectively absorb the laser wavelength but would however, pass the fluorescence wavelength. The two solvents with the best likelihood of accomplishing this are chlorobenzene and o-xylene. Both solutions were tried, but unfortunately, both also absorb the fluorescence wavelength to an equal degree with which they absorb the excitation wavelength.

The upper end of the concentration range of Ga standards are limited when employing a copper electrode as high concentration Ga standard solutions by necessity have a high acid content and will cause a reaction with the copper of the electrode.

Using the same techniques as with lead concentrations in the 1 to 50 $\mu\text{g/mL}$ range were used. The limit of detection was on the order of 0.5 ng.

CHAPTER 6

CONCLUSIONS AND FUTURE STUDIES

Fundamental studies about the sputtering processes of microsamples were carried out in a glow discharge with two different configurations and by two different approaches: Atomic Emission Spectroscopy and Laser Excited Atomic Fluorescence Spectroscopy. In both cases, the atomizer was optimized in such a way that the analyte was sputtered out of the sample holder in a few seconds and the temporal behavior of the emission or fluorescence signal was followed. The figures of merit of both systems showed that a few nanograms by atomic emission or picograms by atomic excited fluorescence can easily be detected in previously dried liquid microsamples. The linear dynamic range of the glow discharge was on the order of two to three orders of magnitude. Although this could be a disadvantage of the atomizer, it did not affect the utilization of the glow discharge in microanalysis where the magnitude of the amount of analyte is covered by the linear part of the calibration curve. The matrix interference study using the two procedures indicated that the sputtering process is affected by concomitant species. For this reason, a more detailed study of this phenomena should be done by a technique like atomic

absorption or atomic fluorescence spectroscopy. Either of these techniques gives information about the ground state population which is necessary to know to clarify how a change in the chemical composition of the analyte affects the sputtering process. The possible formation and ejection of molecular species also should be addressed. In this case, mass spectrometry may be used as the detector for molecular and atomic ions.

The utilization of copper cathode electrodes was evaluated. However, their chemical reactivity may hinder their use with acidic samples. An evaluation of electrodes made of inert materials like glassy carbon could be considered. The volume of the glow discharge chamber was 260 cm^3 . In this volume, as soon as the discharge is initiated a dilution of the atomic cloud in the chamber occurs, reaching a maximum atomic density of $1.12 \times 10^{10}\text{ atoms/cm}^3$ for 1 ng of lead. Improvements in the LEAFS system sensitivity could be achieved by designing a mini glow discharge (1 cm length by 0.4 cm internal diameter) in which the maximum atomic density would be 1.8×10^{13} (3 orders of magnitude higher than used in the present work). This system operated in a stopped flow situation might improve the temporal and spatial probing efficiency, by increasing both, the residence time and atom density.

REFERENCES

1. Schrenk, W.G., *Applied Spectroscopy*, **42**, 1 (1988).
2. Walsh, A., *Spectrochim. Acta*, **7**, 108 (1955).
3. Alkemade, C.T.J.; Milatz, J.M.W. *Appl. Sci. Res.*, **B4**, 289 (1955).
4. L'vov, B.V., *Spectrochim. Acta*, **17**, 761 (1961).
5. Wendt, R.H.; Fassel, V.A., *Anal. Chem.*, **37**, 920 (1965).
6. Wendt, R.H.; Fassel, V.A., *Anal. Chem.*, **38**, 337 (1966).
7. Greenfield, S.; Jones, I.L.I.; Berry, C.T., *Analyst*, **89**, 713 (1964).
8. Greenfield, S.; Jones, I.L.; Berry, C.T.; Bunch, L.G., *Proc. Soc. Anal. Chem.*, **2**, 111 (1965).
9. Montaser, A.; Golightly, D.W., ed., *Inductively Coupled Plasmas in Analytical Atomic Spectrometry*, VCH Publisher, Inc., New York (1987).
10. Caroli, S., *Prog. Analyt. Atom. Spectrosc.*, **6**, 253 (1983).
11. Pashen, F., *Ann. Phys.*, **50**, 901 (1916).
12. Thorton, K., *Analyst*, **94**, 958 (1969).
13. Stirling, A.J.; Westwood, W.D., *J. of Appl. Phys.*, **41**, 724 (1970).
14. Mavrodineanu, R., *J. of Research of the NBS*, **89**, 143 (1983).
15. Korovin, Y. I., *Z. Anal. Khim.*, **16**, 494 (1961).

16. Pevsov, V.Z.; Krasil'shchik, V.Z., Yakovleva, A.F., *Zh. Anal. Khim.*, **23**, 1785 (1968).
17. Zakharov, B.; Myasoedov, B.F.; Karyakin, A.V., *Anal. Khim.*, **28**, 2306 (1972).
18. Harrison, W.W.; Prakash, N.J., *Anal. Chim. Acta*, **49**, 151 (1970).
19. Prakash, N.J.; Harrison, W.W., *Anal. Chim. Acta*, **53**, 421 (1971).
20. Grimm, W., *Spectrochim. Acta*, **23B**, 443 (1968).
21. Boumans, P.W.J.M., *Anal. Chem.*, **44**, 1219 (1972).
22. Stirling, A.J.; Westwood, W.D., *J. Appl. Phys.*, **4**, 246 (1971).
23. Belle, C. J.; Johnson, J. D., *Appl. Spectrosc.*, **27**, 118 (1973).
24. Berglund, B.; Thelin, B., *Analyst*, **107**, 867 (1982).
25. Fang, D.; Marcus, R.K., *J. Anal. Atom. Spectrosc.*, **3**, 873 (1988).
26. Wagatsuma, K.; Hirokawa, K., *Anal. Sc.*, **7**, 289 (1991).
27. Dobrosavljevic, J.S.; Marinkovic, M., *Spectrochim. Acta*, **29B**, 87 (1974).
28. Mehs, D. M.; Niemczyk, T. M., *Appl. Spectrosc.*, **35**, 66 (1981).
29. McDonald, D.C., *Spectrochim. Acta*, **37B**, 747 (1982).
30. Wagatsuma, K.; Hirokawa, K., *Anal. Chem.*, **57**, 2901 (1985).
31. Patel, B.M.; Winefordner, J.D., *Canadian J. Spectrosc.*, **32**, 138 (1987).
32. Wagatsuma, K.; Hirokawa, K., *Anal. Chem.*, **61**, 326 (1989).
33. Wagatsuma, K.; Hirokawa, K., *J. Anal. At. Spectrom.*, **4**, 525 (1989).
34. Wiese, W.L., *Spectrochim. Acta*, **46B**, 831 (1991).
35. Pillow, M.E., *Spectrochim. Acta*, **37B**, 821 (1981).
36. Swift, D.A., *Contemp. Phys.*, **22**, 37 (1981).

37. Ferreira, N.P.; Strausss, J.A.; Human, H.G.C., *Spectrochim. Acta*, **38B**, 899 (1983).
38. Broeckaert, J.A.C., *J. Anal. At. Spectrosc.*, **2**, 537 (1987).
39. Chapman, B., *Glow Discharges Processes*, John Wiley & Sons, New York (1980).
40. Coburn, J.W.; Kay, E., *Appl. Phys. Lett.*, **19**, 350 (1971).
41. Harrison, W.W.; Hess, K.R.; Marcus, R.K.; King, F.L., *Anal. Chem.*, **58**, 341A (1986).
42. Harrison, W.W.; Bentz, B.L., *Prog. Analyt. Spectrosc.*, **11**, 53 (1988).
43. Harrison, W.W.; Barshick, C.M.; Klinger, J.A.; Ratliff P., Mei, Y., *Anal. Chem.*, **62**, 943A (1990).
44. Harrison, W.W., Chapter 3 in, *Inorganic Mass Spectrometry*, Chemical Analysis Series, John Wiley & Sons, New York (1988).
45. VG 900 Glow Discharge Mass Spectrometer, VG Isotopes, Cheshire, England.
46. Gouch, D.S.; Hannaford, P.; Walsh, A., *Spectrochim. Acta*, **28B**, 197 (1973).
47. Butcher, D.J.; Dougherty, J.P.; Preli, F.R.; Walton, A.P.; Wei, G.; Irwin, R.L.; Mitchel, R.G., *J. Anal. At. Spectrom.*, **3**, 1059 (1988).
48. Fraser, L.M.; Winefordner, J.D., *Anal. Chem.*, **43**, 1963 (1971).
49. Weeks, S.J.; Haraguchi, H.; Winefordner, J.D., *Anal. Chem.*, **50**, 360 (1978).
50. Human, H.C.G.; Omenetto, N.; Cavalli, P.; Rossi, G., *Spectrochim. Acta*, **39B**, 1345 (1984).
51. Kosinski, M.A.; Uchida, H.; Winefordner, J.D., *Talanta*, **30**, 339 (1983).
52. Epstein, M.S.; Winefordner, J.D., *Prog. Anal. At. Spectrosc.*, **7**, 67 (1984).
53. Omenetto, N.; Human, H.C.G.; Cavalli, P.; Rossi, G., *Spectrochim. Acta*, **39B**, 115 (1984).
54. Dougherty, J.P.; Preli, F.R., Jr.; Mitchel, R.G., *J. Anal. At. Spectrom.*, **2**, 429 (1987).

55. Bolshov, M.A.; Zyblin, A.V.; Koloshnikov, V.G.; Mayorov, I.A.; Smirnkina, I.I., *Spectrochim. Acta*, **41B**, 487 (1986).
56. Goforth, D.; Winefordner, J.D., *Anal. Chem.*, **58**, 2598 (1986).
57. Leong, M.; Vera, J.; Smith, B.W.; Omenetto, N.; Winefordner, J.D., *Anal. Chem.*, **60**, 1605 (1988).
58. Vera, J.; Stevenson, C.; Smith, B.W.; Omenetto, N.; Winefordner, J.D., *J. Anal. At. Spectrom.*, **4**, 619 (1989).
59. Smith, B.W.; Omenetto, N.; Winefordner, J.D., *Spectrochim. Acta*, **39B**, 1389, (1984).
60. Smith, B.W.; Womack, J.W.; Omenetto, N.; Winefordner, J.D., *Appl. Spectrosc.*, **43**, 873 (1989).
61. Womack, J.B.; Gessler, E.M.; Winefordner, J.D., *Spectrochim. Acta*, **46B**, 301 (1990).
62. Dashin, S.A.; Karpov, Y.A.; Kushlyansky, O.A.; Mayorov, I.A.; Bolshov, M.A., *Spectrochim. Acta*, **46B**, 467 (1991).
63. Travis, J.C.; Turk, G.C.; Watters, Jr.; R.L.; Yu, L.; Blue, L.; *J. Anal. At. Spectrom.*, **6**, 261 (1991).
64. Lunyov, O.S.; Oshemkov, S.V., *Spectrochim. Acta*, **47B**, 71 (1992).
65. Glick, M.; Smith, B.W.; Winefordner, J.D., *Anal. Chem.*, **62**, 157 (1990).
66. Omenetto, N.; Human, H.G.C., *Spectrochim. Acta*, **39B**, 1333 (1984).
67. Alkemade, C.T.J., Chapter 4 in *Analytical Applications of Lasers*, E.H. Peipmeier Ed., John Wiley & Sons, New York (1986).
68. Walsh, A., *Anal. Chem.*, **63**, 933A (1990).
69. Bengston, A., *Spectrochim. Acta*, **40B**, 631 (1985).
70. McCamey, D.A.; Niemczyk, T.M., *Appl. Spectrosc.*, **34**, 692 (1980).
71. Winchester, M.R.; Marcus, R.K., *Appl. Spectrosc.*, **42**, 941 (1988).
72. McNally, J.R Jr.; Harrison, G.R.; Rowe, E., *J. Opt. Soc. Am.*, **37**, 93 (1947).

73. Buger, P.A.; Fink, W., *Z. Phys.*, **236**, 314 (1970).
74. Djulgerova, R.B., Chapter 3 in *Improved Hollow Cathode Lamps for Atomic Spectroscopy*, S. Caroli, Ed., John Wiley & Sons, New York (1985).
75. Caroli, S.; Senofonte, O.; Delle Femmine, P., *Analyst*, **108**, 196 (1983).
76. Broekaert, J.A.C., *Spectrochim. Acta*, **35B**, 225 (1980).
77. Chen, F.; Williams, J.C., *Anal. Chem.*, **62**, 489 (1990).
78. Tseng, J.; Williams, J.C.; Bartlow, R.B.; Griffin, S.T.; Williams, J.C. Jr., *Anal. Chem.*, **63**, 1933 (1991).
79. Chakrabarti, C.L.; Headrick, K.L.; Bertels, P.C., *J. Anal. At. Spectrom.*, **3**, 713 (1988).
80. Patel, B.M.; Winefordner, J.D., *Spectrochim. Acta*, **41B**, 469 (1986).
81. Brackett, J.M.; Vickers, T.J., *Spectrochim. Acta*, **38B**, 979 (1983).
82. Brackett, J.M.; Vickers, T.J., *Spectrochim. Acta*, **39B**, 837 (1984).
83. Strange, C.M.; Marcus, R.K., *Spectrochim. Acta*, **46B**, 517 (1991).
84. Alkemade, C.T.J.; Herrmann, R., *Fundamentals of Analytical Flame Spectroscopy*, John Wiley & Sons, Inc., New York (1979).
85. Browner, R.F.; Boorn, A.W., *Anal. Chem.*, **56**, 787A (1984).
86. Buell, B.E., in *Flame Emission and Atomic Absorption Spectroscopy*, J.A., Dean, T.C., Rains, Eds., Dekker, New York (1969).
87. Snelleman, W.; Rains, T.C.; Yee, K.W.; Cook, H.D.; Menis, O., *Anal. Chem.*, **42**, 394 (1970).
88. Verrept, P.; Vandecasteele, C.; Windels, G.; Dams, R., *Spectrochim. Acta*, **46b**, 99, (1991).
89. O'Haver, T.C., *Anal. Chem.*, **51**, 91A (1979).
90. Manning, D. C.; Ediger, R.D., *At. Absorption Newslett.*, **15**, 42 (1976).

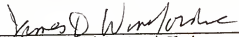
91. Czakow, J., in *Improved Hollow Cathode Lamps for Atomic Spectroscopy*, S.,Caroli, Ed., John Wiley & Sons, New York (1985).
92. Jeans, J., *The Dynamic Theory of Gases*, Dover Publications, New York (1954).
93. Mandelstam, S.L.; Nedler, V.V., *Spectrochim. Acta*, **17**, 855 (1961).
94. L'vov, B.V., *Anal. Chem.*, **63**, 924A (1991).
95. Vamos, Z.; Buuzasi, A. G.; Pasztor, Z., *Talanta*, **38**, 1265 (1991).
96. Falk, H., *J. Anal. At. Spectrom.*, **6**, 631 (1991).
97. Ediger, R.; Peterson, G.; Kerber, J.D., *At. Absorp. Newsl.*, **13**, 61 (1974).
98. Manning, D.C.; Slavin, W., *Anal. Chem.*, **50**, 1234 (1978).
99. Carnrick, G.R.; Slavin, W., *Amer. Lab.*, **Oct.** (1988).
100. Manning, D.C.; Fernandez, F.J., *At. Absorp. Newsl.*, **9**, 65 (1970).
101. Fernandez, F.J.; Manning, D.C., *At. Absorp. Newsl.*, **10**, 65 (1971).
102. Sychra, V.; Svoboda, V.; Rubeska, I., *Atomic Fluorescence Spectroscopy*, Van Nostrand Reinhold Co., London (1975).
103. Kikbright, G.F.; Sargent, M., *Atomic Absorption and Fluorescence Spectroscopy*, Academic Press, London (1974).
104. Ingle, J.D.; Crouch, S.R., *Spectrochemical Analysis*, Prentice Hall, Englewood Cliffs, NJ (1988).
105. Omenetto, N.; Winefordner, J.D. Chapter 3 in *Analytical Laser Spectroscopy*, Chemical Analysis series, John Wiley & Sons, New York (1979).
106. Winefordner, J.D.; Vickers, T.J., *Anal. Chem.*, **36**, 161 (1964).
107. Kirkbright, G.F., *Analyst*, **96**, 609 (1971).
108. Demers, D.R., *Spectrochim. Acta*, **40B**, 93 (1985).
109. Andrews, D.L., *Lasers in Chemistry*, Springer-Verlag, Berlin, Germany (1990).

110. Sacchi, C.A.; Svelto, O., Chapter 1 in *Analytical Laser Spectroscopy*, N. Omenetto, Ed., Chemical Analysis series, John Wiley & Sons, New York (1979).
111. Hecht, J., *The Laser Guidebook*, McGraw-Hill, New York (1986).
112. Vera, J.A.; Leong, B.M.; Omenetto, N.; Smith, B.W.; Womack, B.; Winefordner, J.D., *Spectrochim. Acta*, **44B**, 939 (1989).
113. Omenetto, N.; Winefordner, J.D., *Prog. Anal. At. Spectrosc.*, **2**, 1 (1979).
114. Goforth, D.; Winefordner, J.D., *Talanta*, **34**, 290 (1987).
115. Vera, J.A.; Leong, M.B.; Stevenson, C.L.; Petrucci, G.; Winefordner, J.D., *Talanta*, **36**, 1291 (1989).
116. Smith, B.W.; Farnsworth, P.B.; Cavalli, P.; Omenetto, N., *Spectrochim. Acta*, **45B**, 1369 (1990).
117. Irwin, R.I.; Butcher, D.J.; Takahashi, J.; Wiw, G.; Michel, R.G., *J. Anal. At. Spectrom.*, **5**, 603 (1990).
118. Tremblay, M.E.; Smith, B.W.; Winefordner, J.D., *Anal. Chim. Acta*, **199**, 111 (1987).
119. Tremblay, M.E.; Simeonsson, J.B.; Smith, B.W.; Winefordner, J.D., *Appl. Spectrosc.*, **42**, 281 (1988).
120. Grazhulene, S.; Khvostikov, V.; Sorokin, M., *Spectrochim. Acta*, **46B**, 459 (1991).

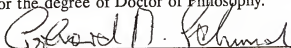
BIOGRAPHICAL SKETCH

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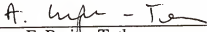
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James D. Winefordner, Chair
Graduate Research Professor of Chemistry

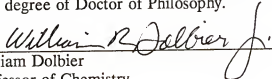
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This dissertation was submitted to the Graduate Faculty of the Department of Chemistry in the College of Liberal Arts and Sciences to the Graduate School and was accepted as partial fulfillment of the requirements for the degree of Doctor of Philosophy.

August 1992

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